Characterization of interfacial integrity and its implication on mechanical behavior of FRP composites

A thesis submitted in partial fulfillment of the requirement for the degree of

Master of technology

In

Metallurgical and Materials Engineering

By

Sanghamitra Sethi

Department of Metallurgical and Material Engineering

National Institute Of Technology, Rourkela

Rourkela-769008

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Under the guidance and supervision of

Prof. B.C. Ray

Department of Metallurgical and Materials Engineering

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National Institute of Technology

Rourkela

CERTIFICATE

This is to certify that the thesis entitled, "**characterization of interfacial integrity and its implication on mechanical behavior of FRP composites**" submitted by Ms **Sanghamitra Sethi in** partial fulfillment of the requirements for the award of Master of Technology Degree in **Metallurgical and Materials Engineering** at the National Institute of Technology, Rourkela (Deemed University) is an authentic work carried out by her under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date-

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CHAPTER-4

RESULTS AND Discussion

Abstract

Fiber reinforced composites (FRP) have been gaining much attention recently because of their use in load carrying parts of new aircraft such as Boeing 787and in non-aerospace applications such as in ships, in retrofitting of structurally deficient bridges, and transportation. Besides this, composite structures in service are typically subjected to different environmental conditions, which may affect their mechanical performance as well as their flammability potential. Water that diffuses in to the composite ends up either in the matrix or at the interphase region. In the matrix, water would act as a plasticizer, increasing the free volume, lowering the glass transition temperature (Tg), and relieving the internal stresses that was built up during processing of the composite. In many cases failures occurs in the interface region due to chemical reactions/plasticizing when impurities (commonly water) penetrate the interface. The continuous change in interfacial chemistry and character under the influence of various environment often leads to a micro changes such as increase of internal voids of the entangling polymer chain, fiber/matrix interfacial bond failure and microcrack formation in to the matrix.

Recently an active area of investigation related to this work is being explored by Temperature Modulated differential scanning calorimetry (TMDSC) and Fourier Transform Infrared Spectroscopy(FTIR-Imaging) ,Ultraviolet spectroscopy (UV),techniques to pin down the causes for a reduce stress transmissibility at the interface. Surface treated glass fiber, carbon fiber and epoxy matrix were used to fabricate micro-composite. Change in FTIR spectra shows alternation and deviation of stoichiometry.The analysis of these suggests that there is a variation in the chemical structure of the matrix from the fiber to the polymer bulk due to different conversions arising from a gradient in the initial composition. And in TMDSC the focus has been emphasized on Tg value which increases when hygrothermal treatment duration is less because of formation of double hydrogen bond and replacing the covalent bond. The increase in Tg value may often lead to the enhanced mechanical properties like interlaminar shear strength and fatigue strength.

CHAPTER -1

BACKGROUND

INTRODUCTION

ADVANCED COMPOSITES

Chapter -1

INTRODUCTION

Background:

Composite materials are as much an engineering concept as they are a specific material. They represent an idea which to the best of knowledge was first recognized in engineering in the composite construction of the latter clipper ships in the middle of the nineteenth century where wooden planning was set on iron frames. The modern term composite arose in the aircraft industry in the middle part of the twentieth century. Its advent can be viewed either as means of using plastics in aircraft construction or as a means of utilizing the stiffness and strength of fibers which were first made in the late 1950s and early 1960s. . The reinforcement of metals through leading to much smaller market sizes than polymer matrix composites has played an important part in the development of the field of composite material generally. In the years after world war II, although the advantages of a composite material were well known to some people, metal dominated the construction market, particularly for aerospace and defence which are often the drivers of new development work at NASA initially intended.

The development of composite materials as an engineering concept and its realization has advanced at the same time as the development of other engineering material.

METAL –MATRIX COMPOSITES

As the name implies, for metal-matrix composites (MMCs) the matrix is a ductile material. This material may be utilized at higher service temperatures than their base metal counterparts; furthermore, the reinforcement may improve specific stiffness, specific strength, abrasion resistance, creep resistance, thermal conductivity, and dimensional stability. Some of the advantages of these materials over the polymer-matrix composites include higher operating temperatures, non-flammability, and greater resistance to degradation by organic fluids. Some matrix-reinforcement combinations are highly reactive at elevated temperature. Consequently; composite degradation may be caused by high-temperature processing or by subjecting the MMC to elevated temperature during service. This problem is commonly resolved either by applying a protective surface coating to the reinforcement or by modifying the matrix alloy composition.

The aerospace industry uses MMCs, structural applications include advanced Al alloy metal-matrix composites, boron fibers are used as the reinforcement for the space shuttle Orbiter, and continuous graphite fibers for the Hubble Telescope.

FIBROUS COMPOSITE:

Composite materials provide stiff, light weight materials of high corrosion resistance, excellent fatigue resistance and may be electrically conducting provided they can be fashioned to shape at acceptable cost there are many applications emerging. They are gaining ground in civil engineering, where the light weight and excellent corrosion resistance makes them the preferred materials for repair of the transportation infrastructure, bridges, roads, tunnels.

A composite, in general, is defined as a combination of two or more components differing two or more distinct phases having recognizable interface between them. The interfaces and interphases between different components in the composite, which is the boundary surface with a discontinuity, have a vital importance in determining the structural properties of the composite. The interfaces and interphases are expected to be proper, i.e. the interaction and adhesion between the components should be at the optimum level in order to distribute the load that is borne by the composite evenly.

Polymers are mostly organic compounds based on carbon, hydrogen and other nonmetallic elements. PMC, are the most developed composite group and they have found widespread applications. This is easily fabricated into any large complex shape, which is an advantage. PMC (also called reinforced plastics) are, in general, a synergistic combination of high performance fibers and matrices. In these systems, the fiber provided the high strength and moduli while the polymer matrix spreads the load and helps resistance to weathering and to corrosion. Thus in PMC, strength is almost directly proportional to the basic fiber strength and it can be further improved at the expense of stiffness. Optimization of stiffness and fiber strength is still one of the unresolved main objectives and is under serious consideration.

In some cases, mainly due to the differences in flexibilities between reinforcing fibers intra and inter fibrillar amorphous zones, severe shear stresses can result in the system, eventually leading to a fatigue crack.

APPLICATION

Composites are the 21st century material to meet the stringent demand of light weight, high strength, corrosion resistance and near-net shapes. Although composites were known to mankind since prehistoric times, the concept and technology have undergone a sea change with better understanding the basics like bonding mechanism between the matrix and fiber.

Modern composites constituents an important class of design and weight efficient structural material that are encroaching every sphere of engineering applications.

Superior directional properties, high specific strength and stiffness properties, design tailoring ease of manufacturing complex shapes as well scores of other attributes make these materials ideally designers' choice[1].

Composite materials and aerospace construction

Fig 1; composite in aerospace

Composite components in Aircraft

Aeronautical constructors have been looking for light weight and robustness from composites since the earlier times.Currently a large variety of composite components are used in aircrafts. Following the more or less important role that composites play to assure the integrity of the aircraft, one can cite the following:

TABLE 1:

Structure components	Control components	Exterior components	Interior components
Wing box	Ailerons	Fairings	Floors
Empennage box	Highlift devices	Karmans	Partitions,buckhead

Characteristics of composites

One can indicate the qualities and weak points of the principal composites used. These serve to justify their use in the corresponding components [2].

TABLE 2:

	Components	Pluses	Minuses
Glass/epoxy, Kevlar/epoxy	Fairings, Leading edges	High rupture strength, Good fatigue resistance	High elastic elongation Maximum temperature 80 °C
Carbon/epoxy	Wing box, fuselage	High rupture resistance No dilation until 600 °C	More delicate fabrication, Material susceptible to lightening.

COMPOSITE IN AUTOMOTIVE INDUSTRY [3]

Composite material is used in a number of applications in the automotive industry due to its temperature resistance, rigidity and fatigue strength. The benefits of using composites include greater fuel efficiency, corrosion resistance, light weight and strength. Composites also provide a low-cost way to help keep designs fresh look.

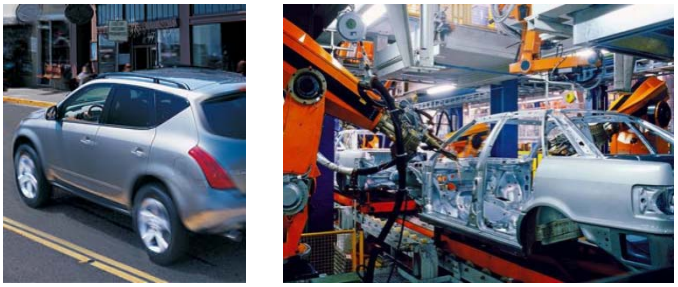


Fig 2 Composite for automotive sector

COMPOSITES FOR CHEMICAL RESISTANCE AND INFRASTRUCTURE APPLICATIONS

Composites are continuing to show utility in applications and systems that demand corrosion-resistant service, as well as applications in infrastructure projects [5].

FIG:3 *Composite towers and ancillary equipment for scrubbers at water treatment facility in Baldwin Park, California*

FIG . A composite rinse tank for processing nutritional products is installed.

FIG composite underground storage tanks are installed at Mobil service stations in Singapore.

Today in North America, over 95% of new tank installations are all composite tanks or composite-overwrapped steel tanks. Proven applications for composites in corrosion-resistant and infrastructure applications will provide a foundation for strong growth for similar uses in the Asia Pacific region. To eliminate economic losses due to leaking hydrocarbons and to better protect the environment, the use of composite underground fuel storage tanks will see a strong surge in growth. This growth will accompany the increased use of automobiles throughout the region. The use of composites for bridges and bridge structures and decks will grow because these products offer better longevity.

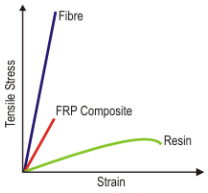


Fig 4: illustrating the combined effect on modulus of the addition of fiber and to the resin matrix.

Loading-- There are four main direct loads that any material in a structure has to withstand: tension, compression, she*ar and flexure.* ***Tension*** Figure 5 shows a tensile load applied to a composite. The response of a composite to tensile loads is very dependent on the tensile stiffness and strength properties of the reinforcement fibres, since these are far higher than the resin system on its own.

Figure 5 – Illustrates the tensile load applied to a composite body.

Compression Figure 6 shows a composite under a compressive load. Here, the adhesive and stiffness properties of the resin system are crucial, as it is the role of the resin to maintain the fibres as straight columns and to prevent them from buckling.

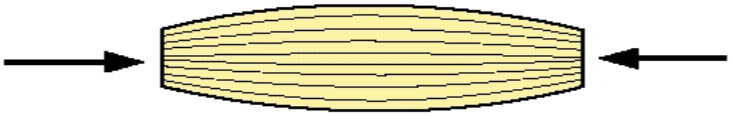


Figure 6 - Illustrates the compression load applied to a composite body.

Shear Figure7 shows a composite experiencing a shear load. This load is trying to slide adjacent layers of fibers over each other. Under shear loads the resin plays the major role, transferring the stresses across the composite. For the composite to perform well under shear loads the resin element must not only exhibit good mechanical properties but must also have high adhesion to the reinforcement fibre. The interlaminar shear strength (ILSS) of a composite is often used to indicate this property in a multiplayer composite ('laminate').

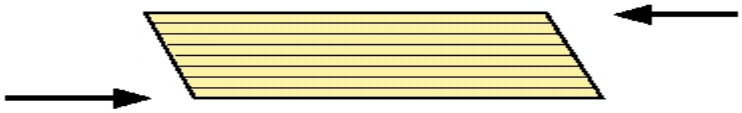


Figure 7 - Illustrates the shear load applied to a composite body.

Flexure Flexural loads are really a combination of tensile, compression and shear loads. When loaded as shown (Figure 8), the upper face is put into compression, the lower face into tension and the central portion of the laminate experiences shear.

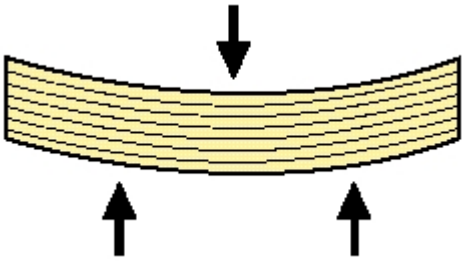


Figure 8 - Illustrates the loading due to flexure on a composite body.

Comparison with Other Structural Materials

Due to the factors described above, there is a very large range of mechanical properties that can be achieved with composite materials. Even when considering one fibre type on its own, the composite properties can vary by a factor of 10 with the range of fibre contents and orientations that are commonly achieved. The comparisons that follow therefore show a range of mechanical properties for the composite materials. The lowest properties for each material are associated with simple manufacturing processes and material forms (e.g. spray lay-up glass fibre), and the higher properties are associated with higher technology manufacture (e.g. autoclave molding of unidirectional glass fibre prepreg), such as would be found in the aerospace industry.

Composites verses Traditional Materials

A judicious selection of fiber,matrix,and interface conditions can lead to a composite with a combination of strength and modulus comparable to or better than those of many conventional metallic material. Composites are superior to metals in specific strength and specific stiffness. Weight reduction is a key consideration in many industries, notably automotive and aerospace. A lighter vehicle because of higher specific properties could mean better fuel efficiency. Polymer matrix composites normally exhibit higher corrosion resistance than metals. However, many polymer-matrix composites tend to absorb moisture from the surrounding environment, resulting in dimensional changes as well as adverse internal stresses within the material. Polymer-matrix composites are more advanced in the fabrication technology and are lower in raw material cost and fabrication cost. When compared to MMCs, PMCs are lower in density.

CONSTITUENT MATERIALS:

INTRODUCTION:

The matrix usually comprises 30%-40% of composite structure. It has a number of functions:

a) It binds the components together and determines the thermo-mechanical stability of the composite,
b) It protects the reinforcements from wear/abrasion and environment,
c) It helps to distribute the applied load by acting as a stress-transfer medium.

As regards the toughness and strength of the composite, the role of the matrix is more subtle and complex than that of the reinforcement involved. Most of the reinforcing components like glass, graphite and boron filles, are all linear elastic and brittle solids, and whenever the stress on them is sufficient to cause unstable flaw growth, they fail catastrophically. and although both reinforcing component and the matrix are brittle, their combination can produce a material that is quite tough (at least much tougher than either of both components alone) via a synergism achieved by a combination of mechanisms that tends to keep cracks and flaws small, isolated and that dissipates mechanical energy effectively[5].

MATRIX POLYMER

THERMOSETTING POLYMER (EPOXY)

Epoxy were first used for composite application in the early 1950's.their good adhesion characteristics with glass,aramid,carbon fibers have resulted in remarkable success as matrices for fiber composites. They also have a good balance of physical, mechanical and electrical properties and have a lower degree of cure shrinkage than other thermosetting resins such as polyester and vinyl ester resins. Epoxies for aerospace composites are generally cured at177 °C (351 °F). Problems with moisture pick-up and loss of some properties may occur at 120 °C to 160 °C with this class of materials. These resins are characterized by the existence of the epoxy group, which is 3-membered ring with 2 carbons and 1 oxygen. This epoxy group is the site of cross-linking and provides for good adhesion with solid substrate like a reinforcement surface. Aromatic groups are often chosen for improved stiffness, thermal stability and higher glass transition (Tg) value. Diglycidyl ether of bisphenol are the most widely used epoxy resin. They have found applications in protective coating, adhesives, sealants, and impregnates, bonding and laminating materials.

Usually epoxy resins are used in conjunction with a curing agent to reduce curing time and to achieve desirable properties such as chemical resistance, thermal stability and glass transition temperature (Tg) are controlled by curing agents. Many of these polymers are considered to be high temperature polymers. However, the term, "high temperature" requires some qualifie… The temperature of 93^0C (199^0F) is frequently cited as a lower limit for continuous use temperature for civil aircraft. About 180^0C (356^0F) is required for skins of supersonic jets and military fighter aircraft. Thermally critical areas of aircraft such as engines have to a temperature of higher than 300^0C (572^0C) missile applications demand short-term

stability in addition to the other properties required for a specific application. The mechanical properties of polymers normally change dramatically and reversibly near Tg/Tm (depending on the crystalline). Even when the Tg/Tm is high, degradation such as thermal oxidation and chemicals attack can change the properties of polymer irreversibly. The presence of aromatic groups in the main chain contributes to high Tg value and also contributes the high tensile and shear properties. Epoxy shows good hot/wet strength, excellent mechanical properties, dimensional stability good adhesion to a variety of reinforcements and better moisture resistance.

Curing of epoxy resin:

The curing of epoxy resins is associated with a change in state from a low molecular weight liquid mixture to a highly cross-linked network. The molecular mobility in the system decreases as the cure proceeds due to cross-linking of several chains into network of infinite molecular weight. The sudden and irreversible transformation from a viscous liquid to an elastic gel is known as gel point. Gelation typically occurs between 55-80% conversion (degree of cure =.55-.80). beyond , the gel point, reaction proceeds towards the formation of one infinite network with substantial increase in cross-link density, glass transition temperature (Tg) and ultimate physical properties.

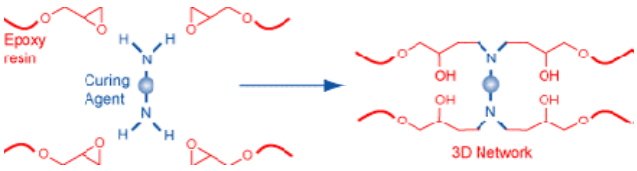


Fig: 9 The curing of epoxy resin with primary amines [7]

During the curing of epoxy resin by multifunctional amines, the amino group and secondary amino group open the oxidant ring and a hydroxyl group is produced [7].

Moisture transport:

One of the major limitations of the epoxy resin is their poor performance in wet environment there has, therefore, been considerable interest in attempting to understand the nature of interaction of water with epoxy resin, particularly the resins used in the fabrication of FRP. These studies have shown that water molecules interact with specific groups within these resins. Water absorption initially plasticizes the matrix.

This is followed by a reduction in tensile modulus and the detachment of the resin from the fiber in the composite. The moisture transport characteristics of a DGEBA system with different stoichiometries have been reported. The moisture absorption is shown to be related to the specific volume and hence to its fractional free volume.

In the glass state, the free volume is apparently in the form of frozen voids and moisture sorption/desorption at the temperature is of the Langmuir type with little/no bond formation. At higher temperature the free volume is generated predominantly through segmental motion occurring above Tg. The Henry's law mode becomes operative and the moisture can now form bonds, two possible roles of heterogeneous morphology have also been highlighted. First, the 2nd stage of absorption process observed distinctly in a number of samples could arise from moisture transport into the more densely cross-linked heterogeneities. Second, the formation of heterogeneity can create voids.

Properties of epoxy:

The properties of epoxy prepolymer such as gel time, viscosity)depend on their backbone structure, molecular weight, molecular weight distribution and the nature of curing agent.

The pure diglycidyl ether of bisphenol-A (EEW=170, Epoxy equivalent weight, i.e weight per epoxide group) generally is not prepared, but prepolymer with EEW of 172-176 are commercially available. Most widely used DGEBA has an EEW of 185-192 [7].

These resins are manufactures by Ciba Geigy (Araldite) and the viscosity of liquid resin ranges from 3000Cps to 19000Cps at 50^0 C .The cured epoxy resins find a variety of applications as adhesives, laminates, sealants, coatings etc. The optimum curing temperature and the thermal stability of epoxy resin depend on the curing agents. Epoxies are used as binders in materials for construction purposes.

Reinforcing agents: *Introduction:*

PMCs are to date the most successful composite material system with a wide range of applications spanning from electronic products such as printed circuit boards to advanced aerospace structures such as in reusable launch vehicles. This is mainly due to the variety of properties that can be achieved by combining fibers of glass, carbon, aramid and polyethylene, together with mixture of these, using thermosetting polymer as matrix materials.

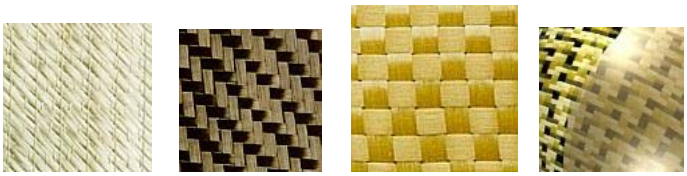


FIG-10 It shows different types of reinforcement

The fiber configuration or architecture (short, long, straight, woves, braided, laminated etc.) and the fiber surface treatment for the desired interface characteristics determine the final properties and the composite durability [8]. The breaking strength and the stiffness of a fiber of given chemical constitution can be understood in terms of the geometric form which often governs the strength, molecular construction and internal structure of the fiber which governs the stiffness. The stiffness of the fiber-along its axis-can be understood with some precision-say within 50% from knowledge of the binding forces between the component atoms. The fibers are strong because the surface is likely to be smooth-in general the thinner the smoother [9]. The factors controlling the strength and stiffness of fibers were recognized in the 1960s and very stiff and strong fiber of boron and graphite were made for the 1st time. They were strong and stiff, but also because they were made from chemical elements of low molecular weight, they are much less dense then most metals. A key feature of composite material is that they may be tailored so that their properties match the required performance. Approximately 1.8 Mt of E-glass fiber is manufactured annually for use in composites and their represents some 80% of the continuous glass filament produced. Some 30% is used to reinforce thermoplastics and 50% goes into continuous and long-fiber reinforced thermosets, which are the traditional composite market. The remaining 20% is used in various textile forms.

GLASS FIBERS AND SILANE COUPLING AGENTS: A) Structure and Properties of glass fibers:

A variety of chemical compositions of mineral glasses have been used to produce fibers. The most commonly used are based on silica (SiO_2)with additions of oxides of calcium,Al ,Fe. The polyhedron network structure of sodium silicate glass is shown in Fig

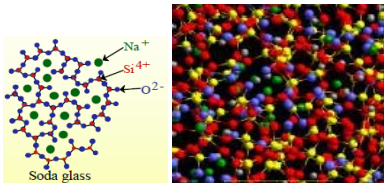


Fig :11 Polyhedral network structure of glass fiber

The three dimensional network of structure of glass results in isotropic properties of glass fibres, in contrast to those of carbon and Kevlar aramid fibers which are anisotropic. The elastic modulus of glass fibers measured along the fiber axis is the same as that measured in the transverse direction, a characteristic unique to glass fibers [5].

Carbon fiber:

High strength, high modulus carbon fibers are manufactures by treating organic fibers (precursors) with heat and tension, leading to a highly ordered carbon structure. Carbon fibers possess very high specific properties and it is this which makes them so attractive as the reinforcing element in a composite material [6].

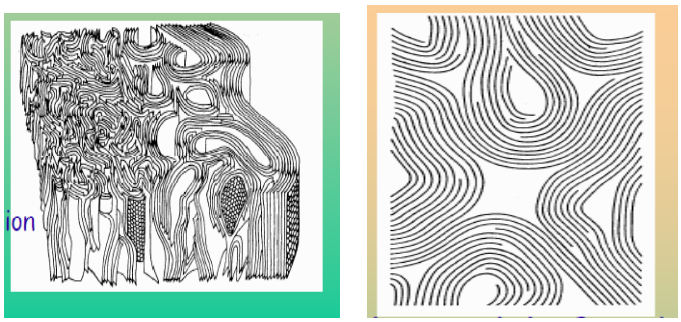


Fig :12 a) Model of skin-core organization of carbon –fiber.,(b) Lamellar model of carbon in cross-section. Carbon Fiber –matrix interphase:

The properties of the material between the fiber reinforcement and the polymer matrix have a significant influence on the mechanical properties of CFRP. To produce a high-modulus composite requires adequate adhesion between the fiber and the matrix. The fiber-matrix interface is also important in influencing load transfer in the vicinity of a broken fiber and therefore has a role in determining the tensile strength. The transition region, known as the interphase, between the bulk fiber and the bulk matrix is extremely complex. Constituents of the interphase might include a modified fiber surface or a coating of a polymer present to ensure compatatibility with the matrix polymer. In addition, the presence of the fiber surface may affect the cure to thermosets, resulting in a chemically different polymer in the interphase region, or may affect the morphology of semicrystalline thermoplastics [10]. ***The nature of the interface depends not only on the matrix but also on the fiber surface treatment and sizing.***

The failure mode at the interface was cohesive at the high levels of treatment, suggesting that the interface has been optimized at these levels, with shear strength of about 70MPa. The measured yield strength of the bulk 922 resin was 195 MPa. It would be of interest to be able to comment whether these data suggest that,1) interface strength being controlled by the matrix shear strength or 2) the interface is of a significantly different composition to the bulk matrix and hence has different mechanical properties. ***For current stiffer and strong fibers and tougher thermosetting resins, interfacial shear strengths generally seem to lie between 40 and 60 MPa.***

Aramid fiber:

Several types of interfaces can exist in composite materials, including mechanical, chemical, and physical interfaces. Mechanical interfaces are realized by the “key and lock” mechanisms. Primary factors controlling this type of interface are fiber surface roughness, porosity, surface morphology, and matrix pore-filling capabilities. This type of interface plays a very important role in ceramic matrix composites by providing a necessary degree of matrix debonding when the composite is under loading conditions, which can lead to the optimization of the composite mechanical properties.

CHAPTER -2

LITERATURE SURVEY

INTERFACE AND INTERPHASE

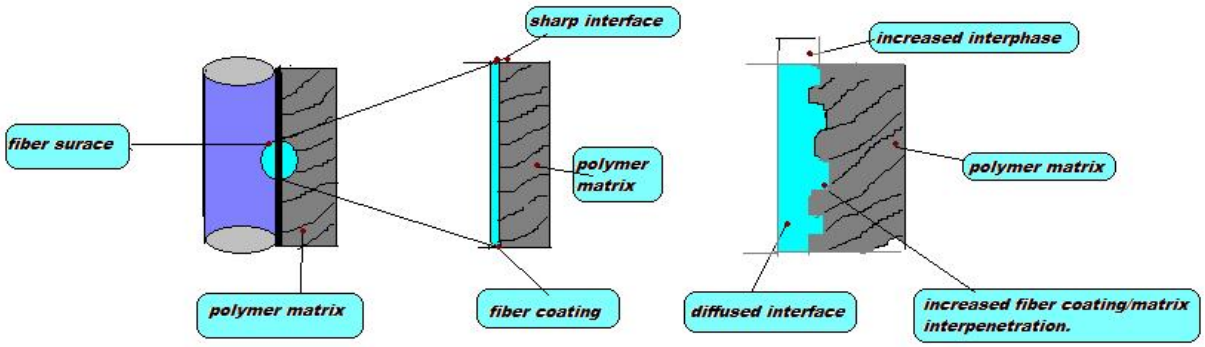
ASSESSMENT OF MECHANICAL BEHAVIOR

Chapter 2

Literature survey

2.1 *INTERFACE AND INTERPHASE*

Interfacial Analysis: The fiber/matrix interface is a key component of FRP. The small dimensions of the interfacial region make its physical and chemical characterization a challenging problem. Although the concept of a "perfect" interface took root in conventional mechanics, which has treated the interface as a infinite thin layer with no physical properties of its own, it is generally agreed today that the interfacial region of a composites extends a considerable distance from the fiber surface into the matrix, and has a complex chemical structure a broad range of physical properties. The subject of interfacial analysis encompasses both the chemical and mechanical characterization of this interfacial region, which is frequently called the "interphase".



(a) (b) (c)

Fig 13 a) A fiber-matrix arrangement b) A fiber coating and sharp interface at fiber-matrix interface (c) A diffused interface between matrix and fiber coating causing an increase in the interphase thickness.

Durability of glass-fiber/epoxy composites is dictated by the durability of the components; glass fiber, matrix and the interface. Environmental attack by moisture, for example, can degrade the strength of the glass fiber; plasticize, swell, or microcrack the resin; and degrade the fiber/matrix interface by either chemical or mechanical attack. The scientific study of composite interfaces began in the United States in 1963 as a result of 2 meeting.

2.2 Chemical aspects of different fiber on the basis of INTERFACE region

Glass fiber-reinforcement

Silane agents are intended to act as a protective coating for glass fiber surface and as a coupling agent to promote the adhesion with the polymer matrix. In the chemical bonding theory, the bifunctional silane molecules act as a link between the resin and the glass by forming a chemical bond with the surface of the glass through a siloxane bridge, while its organofunctional group bonds to the polymer resin [5].

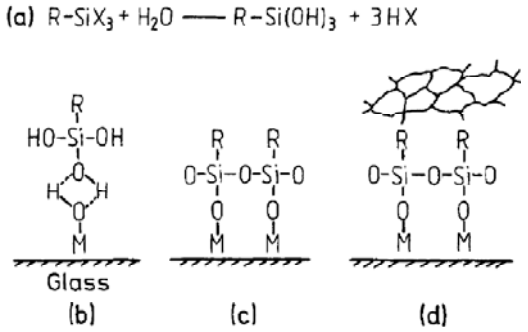


Fig 14 Functions of a coupling agent: a) Hydrolysis of organosilane to corresponding silanol; b) Hydrogen bonding between hydroxyl groups of silanol and glass surface c) Polysiloxane bonded to glass surface d) Organofunctional R-group reacted with polymer [5]. A number of factors affect the microstructure of the coupling agent which, in turn controls the mechanical and physical properties of the composites made therewith. They are the silane structure in the treating solution and its organofunctionality, acidity,drying conditions and homogeneity, the topology and the chemical composition of the fiber surface. In particular, with the development of FTIR spectroscopy,it is possible to observe the chemical reaction in the silane interface region during cure.

Aramid fiber reinforcement:

Aramid make up a 3rd category of reinforcement fiber for polymer matrix composite. Neither the coupling agents used on glass nor the surface oxidation treatments found suitable for carbon have successfully enhanced the interfacial strengths of aramid reinforcement. This have large positive coefficient of thermal expansion in the transverse direction resulting in shrinkage away from the matrix during cooling down from the processing temperature.

Promising improvement in the interfacial properties of aramid fibers have been obtained by plasma treatment. The failure mode changed from predominantly interphase cracking to fiber splitting and matrix cracking, evidence for bonding between the surface amine groups and the epoxy resins.

2.3 Mechanical Aspects of interface region

The mechanical performance of a FRP depends on the strength and modulus of its principal constituents, the fiber and the matrix bond in transferring stress through the material. The elastic modulus of a composite loaded statically in tension will be dominated by the fibers aligned in the direction by stress. As applied stress is increased, the interface between the low modulus matrix and the high modulus fiber becomes the most highly stressed region of the composites, thus the quality of the interface affects the ultimate stress and strain of a unidirectional composites even when loaded in pure tension parallel to the fibers [10].

CHARACTERISATION OF THE INTERFACE:

PHYSICOCHEMICAL ANALYSIS:

Adhesion physics is a well-established science, with obvious applicability to composite interfaces.

Wetting studies: A stable interface can occur only if its formation yields a reduction in the surface free energy of the fiber or other solid phase. Increased instrumental sophisticated has permitted much elaboration on this early theme by among others, the research groups headed by H.Ishida and J.L.Koeing at case Western Reserve University.

Progressing outward from the glass surface, these are:

1. Chemically reacted monolayer
2. A tightly bound chemisorbed layer
3. Loosely bound chemisorbed layer
4. Physisorbed layer, which is removable with organic solvents.

Surface treatment of fibers and effects on composite properties.

The interlaminar shear, flexural, and tensile strengths are increased as the principal effects of fiber surface treatment on composite properties. The enhancement of these strength properties depend on the fiber elastic modulus, the degree of surface treatment and the type of resin and curing agent used. The largest improvement in ILSS is obtained for high modulus fibers.

2.4 Fiber / matrix adhesion

Fiber-matrix adhesion is viewed as a necessary criterion for achieving acceptable composite properties. The patent literature contains numerous chemical formulations, processes, and procedures designed to increase fiber-matrix adhesion levels so that acceptable composite mechanical properties could be achieved. As our understanding of the relationship of fiber-matrix adhesion to composite mechanical properties has increased, it has become apparent that adhesion not only is necessary, but also, if properly designed, can enhance the composite mechanical properties and performance.

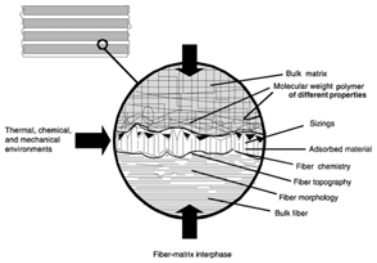


FIG: 15 Schematic diagram of the fiber-matrix interphase and some of the factors that contribute to its formation [12].

2.5 Study of moisture ingression by determination of Tg

Moisture absorption in polymer composites leads to changes in the thermo physical, mechanical and chemical characteristics of polymer matrix by plasticization and hydrolysis [13]. The presence of moisture and the stresses associated with moisture-induced expansion may cause lowered damage tolerance and structural durability. Water pick-up kinetics and mechanical test (ILSS) are supposed to be indicative of evaluating adhesion chemistry at the fiber/matrix interfaces and the integrity of composites. An attempt has been made here to evaluate the effect of thermal stress on shear strength of moisture induced swell composites.

The common damage modes are matrix cracking, delamination growth and fiber fracture [14]. Plasticization and swelling are among the adverse consequences of absorbed water. Plasticization induces plastic deformation in addition to lowering the Tg. whereas swelling is related to the differential strain which is created by the expansion force exerted by the liquid while stretching polymeric chains. These two damage mechanisms are believed to generate capillarity in polymeric composites. The stress transfer efficiency from the matrix to the fibers, the stress build-up in broken fibers and the redistribution of the stresses in the neighboring intact fibers are all controlled by the interfacial strength and integrity [15]. Microcracking induced by environment is a long standing problem in polymer composites. Cracking leads to mechanical degradation of fiber reinforced polymer composites. A typical cured resin may absorb between 4.5 and 7.0 wt % of water at equilibrium, which may reduce the glass transition temperature (Tg) by 80-140 °C [16].

From the practical point of view, the glass transition is a key property since it corresponds to the short-term "Ceiling" temperature, above which there is a catastrophic softening of the material occur. It also considered as a "floor" temp, because the polymerization (cure) exhibits a very slow/severe negligible rate in the glass state [7]. For polymers to endure higher temperature (>230 °C) for a long period, the polymers must have high Tg and good thermal stability. The mechanical properties of polymers normally change dramatically and reversibly near Tg or Tm. The presence of aromatic groups in the main chain contributes to high Tg value and also contributes to high tensile and shear properties. Since the Tg corresponds to a mobility change in a polymer and has a definite free volume associated with it.

2.6 Glass transition temperature (Tg) and relaxation time

"Relaxation time" is a time constant for a system to return to equilibrium in response to a sudden disturbance, like a pressure jump/temperature. In the glassy state relaxation times becomes very large, making the continuation of the polymerization reaction difficult. Due to this long relaxation times, and are not free to absorb the energy of the impact by chain slippage, so almost all of the impact energy must be absorbed by the chain backbones. If failure occurs, it will be by instantaneous brittle fracture. The relaxation may be considered as an inherently non-exponential process, usually involving the stretched exponential relaxation function [17].

In a glassy state, crazing is a major factor in stress relaxation and in creep. Crazing in glassy polymers greatly increases the creep and stress relaxation. At temperature well below Tg where polymers are brittle, their molecular weight has a minor effect on creep and stress relaxation. This occurs more easily in low-molecular-weight polymers, which can increase the creep and stress relaxation rate before failure takes place. Once craze begins to form at a flaw, the polymer chains in that region reorient in response to both the applied load and the reduced cross-sectional area/stress concentration at that point due to the flaw [18].

2.7 Molecular theory of polymer

The interest in environmental effects on composites was rekindled in the mid-1990s due to new applications contemplated for these materials, which combine severe exposures and higher design requirements. These new applications occur in the offshore oil industry, in civil infractures and in naval submersibles. The simplest model for the diffusion of solvent into a solid is given by linear Fick's Law (1885). Accordingly, the flux of the solvent, is proportional to the negative of) concentrations gradient ∇ m. In the one dimensional case we have

$$F=-D\partial m/\partial x$$

Where D is the diffusion coefficient. The negative sign in this equation indicates that the flux is directed from high concentration to low concentrations region [7]. Experimental evidence indicates that for most of polymeric composite materials the hygrothermal behavior is Fickian nature. Thus, the absorption and desorption curves when plotted (time) are always concave toward the (time) axis and asymptotically reach the equilibrium value. But the diffusion behavior of glass polymer doesn't obey the Fick's law. Non-fickian behavior is also a material characteristic. Deviation from Fickian's law becomes more pronounced at elevated temperature and for materials immersed in liquids [19].

Causes and modes for Non-Fickian Diffusion:

There is a host of possible reasons for non-Fickian diffusion in polymers and yet additional probable causes when considering polymeric composites. The fact that glassy polymers, with their highly complex molecular configurations, exist in a nonequilibrium thermodynamic state accounts for their inherent time-dependent behavior. Consequently, the time-dependent diffusion process occurs conjointly with the time-dependent mechanical response of polymers, namely creep and relaxation. Accordingly, the polymer requires time to approach its new equilibrium state commensurate with externally imposed boundary conditions [10].

2.8 Free volume theory

Recent advances in polymer Engineering and technologies makes the applications of polymer materials versatile in various fields, ranging from traditional to high tech industries. Free volume is the fraction of the volume not occupied by the polymer. This concept has found uses in discussing physical properties such as viscosity, diffusion in liquids, viscoelasticity, electrical conductivity, the glass transition and plastic yielding.

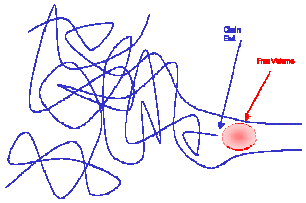


Fig: 16 Schematic view of free volume in polymer.

Computation of free volume theory

Free volume distribution has been studied theoretically by using kinetic theories and molecular dynamics. Experimental probes for free volume at molecular and atomic scale is possible using small angle diffraction, fluorescent spectroscopy and position annihilation lifetime spectroscopy, which has emerged as the unique method providing resolution of a few Anstroms.it has been widely accepted that the gas diffusion through a glassy polymer can be related to the fractional free volume of the polymer through the DOOLITTLE relation,

Where f-fractional free volume

A &B are constant.

As the free volume increases and pores becomes connected, this relation doesn't adequately model the experimental data.by adding newly available high free volume polymer that is PARK & PAULI'S an empirically relation is,

$$D=\alpha \exp(\beta f)$$

Where α & β are constants.,is shown all of the data well.

It is known that as the fractional free volume in polymers increases the pores becomes interconnected and provides a flow through path for the permeating gas which has commonly been identified with a pore flow diffusion process. Gas molecules are free to move within the maze to connected pores.

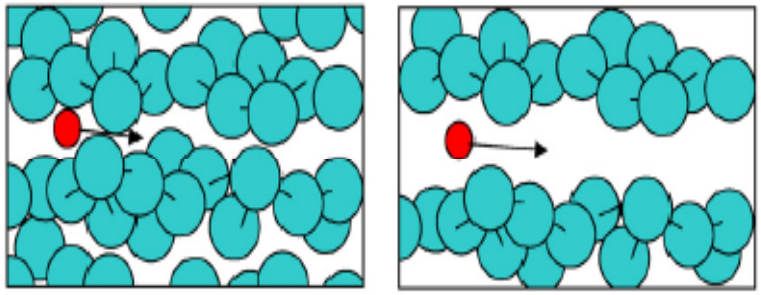


Fig- 17 schematic diagram of different diffusion process (a)closely packed glassy polymer (b)high free volume glassy polymer.

Water penetration in composite materials of different interfacial strengths has been studied and explained as the result of two parallel processes, i.e., diffusion through the polymer matrix and through a network of micro-channels formed along the imperfectly bonded polymer-fiber interface. Such channels along the exterior of the loose fiber are presumed to contribute mesoscopic ‘‘free volume’’ to the composite which is conductive to diffusion. An analytical method based on an adaptation of the free volume theory approach is proposed for estimating the incipient looseness and any further interfacial relaxation caused by water absorption in composite materials.

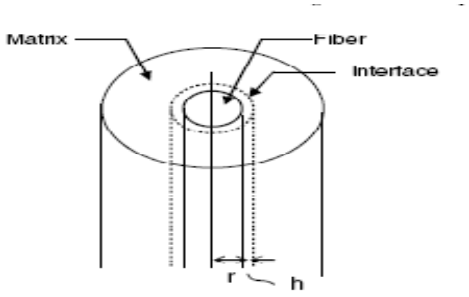


Fig- 18 Idealized represtation of interfacial free volume of annular thickness h,around an imperfect bonded fiber radius r in a composite.[]

2.9 Free volume and Tg

Upon a gradual temperature decrease polymers (especially whose with irregular structure or composed of monomers fairly different in their structure and volume) form a glassy state (i.e. undergo the glass transition). The glass transition temperature is a function of molecular architecture, monomer units, presence of impurities or low molecular weight species and the rate of temperature changing [20]. Normally there is some free space between polymer monomers even in melt. In general one can distinguish between the total volume and the occupied volume. The difference between these two considered to be a free volume. The amount of the free volume changes with temperature.

2.10 Degree of crosslinking and its impact

A small no. of chemical cross-links act about the same as entanglements, but the cross-links do not relax/ becomes ineffective at high temperature. Thus cross-linked elastomers show rubberlike elasticity and recoverable deformation even at high temperature and for long times after being stretched or deformed [21].The modulus on the rubbery region increases with the number of cross-link points or equivalently, as the molecular weight between cross-links Mc decreases. In addition to raising the rubbery modulus, cross-linking produces 3 other effects, first when the cross-link density becomes fairly high, the glass transition temperature (Tg) is increased, so the drop in the modulus becomes shifted to higher temperature/ longer times. Second, the transition region is broadened, with the modulus dropping as a lower rate and platenuing at a higher level[22].

Widely spaced cross-links produce only slightly restrictions on molecular motion, so that Tg tends to be close to that of the uncross-linked polymers. As the cross-link density is increased, molecular motion becomes, more restricted and the Tg of the cross-linked polymer chain rises. The final reason for the broadening is that the nature of the polymer backbone has changed and the highly cross-linked system has become a copolymer. Cross-linking has rather little effect on the magnitude of the modulus in the glassy state (i.e at very short times/at temperature below Tg). Both increases and decreases have been observed [23].

2.11 Assessment of Engineered Interface

The local response of the fiber-matrix interface within the composite during fracture is particularly important. If the interface in a composite is to be designed to resist fracture and thus to enhance the damage tolerance prior to failure, it is necessary to understand the basic failure mechanisms or origin of fracture toughness[24]. The cracks in composites can propagate preferentially along the fiber-matrix and laminar interfaces or transversely right through the fiber-matrix, depending on the properties of the interface. When the crack presents in the matrix the following failure mechanisms may be takes place:

1. Matrix fracture 2: Fiber-matrix interface debonding 3:Post-debonding friction

4: Fiber fracture 5: Fiber pullout 6: Stress redistribution [25].

All these mechanisms, except fracture of fibers and the matrix, are a direct consequence of shear failure at the imperfectly bonded fiber-matrix interface. A weak interface bond is detrimental to some mechanical properties, particularly the longitudinal compressive strength and transverse tensile strength [6].

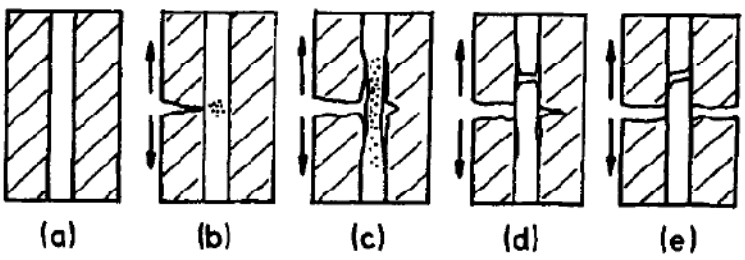


Fig : 19 Model of crack-fiber interaction in a simple composites[6].

The ability of a composite material to arrest cracks through longitudinal splitting contributes to the overall improvement in energy absorption capability and thus its fracture toughness.

Surface treatments of fiber and particle reinforcements are common methods to improve the general adhesion properties by increasing electrostatic interactions and /or facilitating chemical bonding between the constituents [26]. Many applications reveal a sensitivity of resin matrix and fiber/matrix interface to both environmental degradation, with interactions between various mechanisms being possible. With the increasing applications of these materials, more and more assessment is needed to get a better understanding of interfacial bonding of the materials. The environmental action, such as high moisture and high temperature, can limit the usefulness of polymer composites by deteriorating mechanical properties during service[27]. Usually, it is accepted that the interphase region has a thickness of 100 to 500 nm. Interface between fiber and matrix is believed to play an important role in composite properties[28]. The effectiveness of load transfer at the interface depends upon the extent of chemical and mechanical bonding. In addition, composites properties are further compromised by structural defects such as voids, impurities and microcracks which tend to concentrate at the interface region. Therefore, the degradation at the interface area is of specific interest in understanding the failure modes of polymer composite[29].

2.12 Assessment of mechanical behavior (implication of thermal shock and thermal spike)

Hybrid composite

Different types of fibers can be incorporated into a matrix material to produce a hybrid fiber composite. Typical hybrid fiber composites are made from glass that are added to brittle carbon fiber composites to enhance the fracture toughness resulting from the toughening mechanisms associated with the ductile fibers, while maintaining a high strength and high modulus gained from carbon fibers[30]. The effect of toughening relies heavily on how the hybrid fibers are mixed and the ply layup is arranged.

Hybridization provides materials designers with an added degree of freedom in tailoring composites to achieve a better balance of stiffness and strength, increased failure strain, better damage tolerance, improved ability to absorb impact energy and possibly a significant reduction in cost[31]. Hybrid composites are attractive structural materials, because the composite properties can be tailored to requirements, other characteristics of hybrid composite are cost effective utilization of different fiber materials, possible weight savings, reduced notch sensitivity, improved fracture toughness, larger fatigue life and improved impact resistance[32]. In general, hybrid effect leads to the enhancement of the failure strain and strength than that estimated using classical lamination theory and the various failure strain criteria[33]. The maximum tolerated was the load corresponding to either a gross fiber failure at the back surface or an inter laminar crack across the composite sample[34]. Also the intermixing of glass and graphite fiber plies helped decrease the sudden catastrophic failure mode. Chamis et al have studied glass/carbon hybrid composites and have observed that hybrid composite failed under impact by combined fracture modes: fiber breakage, fiber pullout and interplay delamination [35].

CHAPTER-3

FTIR-Imaging

ATR-FTIR

TMDSC

AFM

UV

SEM

MATERIALS AND EXPERIMENTAL

CHAPTER-3

TECHNIQUES

3.1 FOURIER TRANSFORM INFRARED SPECTROSCOPY (FTIR)

Infrared (IR) spectroscopy is one of the most common spectroscopic techniques used by organic and inorganic chemists. Simply, it is the absorption measurement of different IR frequencies by a sample positioned in the path of an IR beam. The main goal of IR spectroscopic analysis is to determine the chemical functional groups in the sample. Different functional groups absorb characteristic frequencies of IR radiation. Using various sampling accessories, IR spectrometers can accept a wide range of sample types such as gases, liquids, and solids. Thus, IR spectroscopy is an important and popular tool for structural elucidation and compound identification[36].

BASIC PRINCIPLE:

Except at very, very low temperatures, all molecules are in motion in some manner. Molecules *translate* (move from place to place), they *rotate* in space, and, importantly for this experiment, they *vibrate*. In the case of the triatomic, bent molecule SO2, the seemingly random vibrations of the molecule can actually be broken down into three so-called "normal modes" of vibration (*Figure 1*). These normal modes are a bending of the molecule and two stretching motions. In the bending motion, the O atoms wag in and out. In one stretching motion, the two O atoms move symmetrically in and out relative to the S atom, whereas in the other motion the two O atoms move unsymmetrically in and out. That is, as one moves out the other moves in, and vice versa. Bending and stretching motions occur in all molecules. The only difference is that more

complex molecules have many more bending and stretching motions.

IR Frequency Range and Spectrum Presentation

Infrared radiation spans a section of the electromagnetic spectrum having wave numbers from roughly 13,000 to 10 cm^{-1}, or wavelengths from 0.78 to 1000 μm. It is bound by the red end of the visible region at high frequencies and the microwave region at low frequencies. IR absorption positions are generally presented as either wave numbers ( ) or wavelengths (l).

Wave number defines the number of waves per unit length. Thus, wave numbers are directly proportional to frequency, as well as the energy of the IR absorption. The wave number unit (cm–1, reciprocal centimeter) is more commonly used in modern IR instruments that are linear in the cm–1 scale. In the contrast, wavelengths are inversely proportional to frequencies and their associated energy. At present, the recommended unit of wavelength is μm (micrometers), but μ (micron) is used in some older literature. Wavenumbers and wavelengths can be interconverted using the following equation:

$$\square \text{ (in cm}^{-1}) = 1/\lambda(\text{in } \mu\text{m}) \ 10^4$$

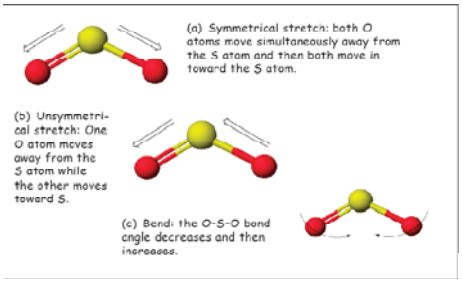
IR absorption information is generally presented in the form of a spectrum with wavelength or wave number as the x-axis and absorption intensity or percent transmittance as the y-axis

Transmittance, *T*, is the ratio of radiant power transmitted by the sample (*I*) to the radiant power incident on the sample (*I*0). Absorbance (*A*) is the logarithm to the base 10 of the reciprocal of the transmittance (*T*).

$$A = \log_{10}(1/T) = \log_{10} T = \log_{10} I/I_O$$

The transmittance spectra provide better contrast between intensities of strong and weak bands because transmittance ranges from 0 to 100% *T* whereas absorbance ranges from infinity to zero. The analyst should be aware that the same sample will give quite different profiles for the IR spectrum, which is linear in wavenumber, and the IR plot, which is linear in wavelength. It will appear as if some IR bands have been contracted or expanded.

THEORY OF INFRARED SPECTROSCOPY:



Fourier Transform Spectrometers

Fourier transform spectrometers have recently replaced dispersive instruments for most applications due to their superior speed and sensitivity. They have greatly extended the capabilities of infrared spectroscopy and have been applied to many areas that are very difficult or nearly impossible to analyze by dispersive instruments. Instead of viewing each component frequency sequentially, as in a dispersive IR spectrometer, all frequencies are examined simultaneously in Fourier transform infrared (FTIR) spectroscopy.

Spectrometer Components

There are three basic spectrometer components in an FT system: radiation source, interferometer, and detector. A simplified optical layout of a typical FTIR spectrometer is illustrated in Fig. 15.4. The same types of radiation sources are used for both dispersive and Fourier transforms spectrometers. However, the source is more often water-cooled in FTIR instruments to provide better power and stability. In contrast, a completely different approach is taken in an FTIR spectrometer to differentiate and measure the absorption at component frequencies. The monochromator is replaced by an interferometer, which divides radiant beams, generates an optical path difference between the beams, and then recombines them in order to produce repetitive interference signals measured as a function of optical path difference by a detector. As its name implies, the interferometer produces interference signals, which contain infrared spectral information generated after passing through a sample. The most commonly used interferometer is a Michelson interferometer. It consists of three active components: a moving mirror, a fixed mirror, and a beamsplitter (Fig. 15.4). The two mirrors are perpendicular to each other. The beamsplitter is a semi reflecting device and is often made by depositing a thin film of germanium onto a flat KBr substrate. Radiation from the broadband IR source is collimated and directed into the interferometer, and impinges on the beamsplitter. At the beamsplitter, half the IR beam is transmitted to the fixed mirror and the remaining half is reflected to the moving mirror. After the divided beams are reflected from the two mirrors, they are recombined at the beamsplitter. Due to changes in the relative position of the moving mirror to the fixed mirror, an interference pattern is generated. The resulting beam then passes through the sample and is eventually focused on the detector.

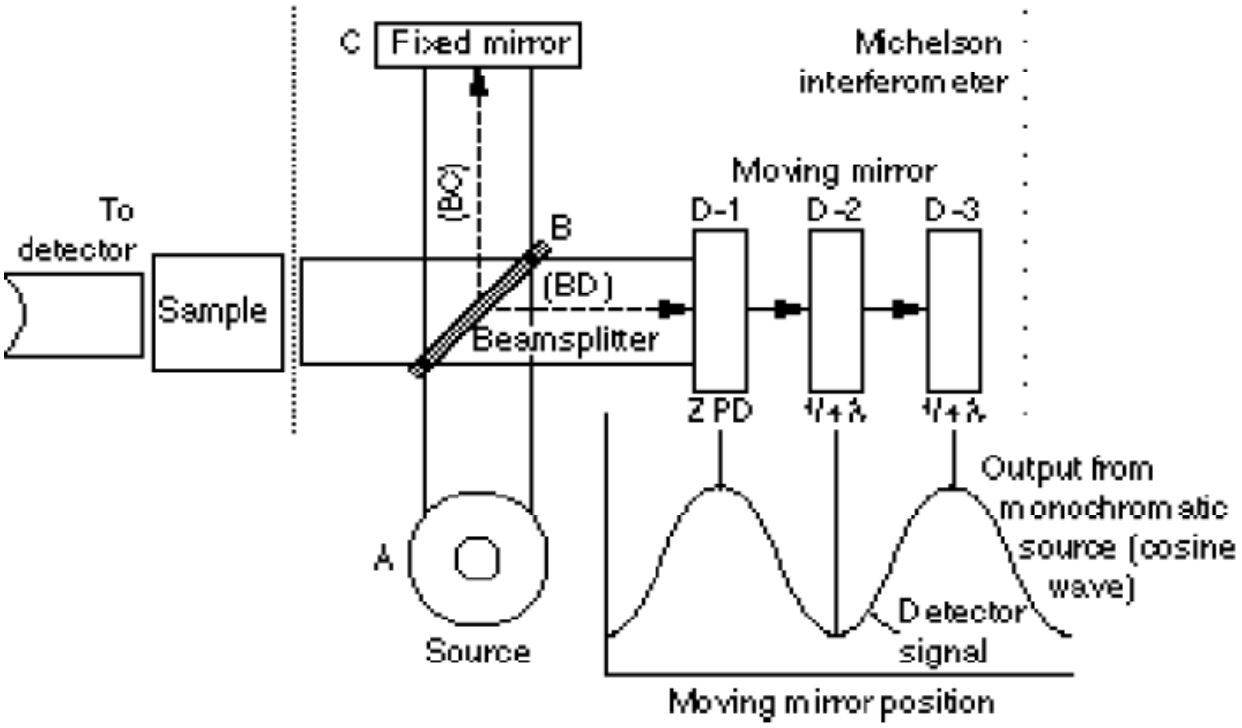


FIG-20 Arrangement of FTIR Spectroscopy

The IR region is commonly divided into 3 smaller areas:

Table 3-

	Near IR	Mid IR	Far IR
Wave Number	13,000-4000 cm^{-1}	4000-200 cm^{-1}	200-10 cm^{-1}
Wave length	0.78-2.5μm	2.5-50μm	50-1000μm

Characteristic Patterns in Infrared Spectrum

Just as each person has a unique set of fingerprints, each chemical compound has a unique infrared spectrum. If you have available an enormous library of reference spectra, and a powerful computer, in principle you could match the spectrum of an unknown compound with the library and uniquely identify the compound. This is in fact done—the Chemistry Department has an infrared system with this capability.

But what if you have a spectrum of a completely new compound, or one that is not in your database? It turns out that different parts of a molecule—its *functional groups*—give rise to infrared vibrations in reasonably well defined regions of the infrared region. For example, as *Figure 3* shows, stretching vibrations of bonds to H usually occur at higher energies, triple bonds have higher energy stretching vibrations than those of double bonds, whereas bending vibrations occur at lower energies. Extensive experience has led to the compilation of correlation tables. For example, chemists know that the stretching motions of bonds commonly found in organic compounds occur in the ranges given in the table below.

Table -4

BOND	Frequency (cm^{-1})	Shape and intensity
O-H	3650-2500	Often broad,strong
N-H	3400-3200	Sharp,Variable
-C-H	2960-2850	Sharp,Medium
=C-H	3100-3000	Sharp,Mediun
C=C	1680-1620	Sharp,Variable
C=O	1800-1630	Sharp,Strong
C-O	1300-1000	Sharp,Strong

3.1 B ATTUNATED TOTAL REFLECTION (ATR-FTIR)

BASIC PRINCIPLE

Attenuated Total Reflectance (ATR) spectroscopy has been used to measure interdiffusion for a number of polymer systems. This technique is attractive for several reasons. It is easy, simple and nondestructive, and the penetration depth ranges between 0.1 to 10 mm. Any concentration change within the penetration depth due to diffusion of one polymer in another one can be observed in situ. The diffusion of each polymer can then be followed independently, provided that the compounds have some infrared distinguishable absorption bands. It is possible to work in a broad range of temperatures (below and above the Tg) and with a wide variety of interface combinations (amorphous, crystalline, thermoplastic, thermoset polymers, different molecular weights, etc). The ATR method offers the advantage of measuring the diffusion coefficients over a wide range of values: 10-5 – 10-16 cm2sec-1, as well as characterizing chemical interactions occurring within the polymeric system.

3.1 C TEMPERATURE MODULATED DIFFERENTIAL SCANNING CALORIMETRY (TMDSC)

BASIC PRINCIPLE AND WORKING CONDITION

TMDSC is a technique for measuring the energy necessary to establish a nearly zero temperature different between a substance and an inert reference material as the two specimens are subjected to identical temperature regimes in an environment heated / cooled at a controlled rate.

The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as, phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature. Whether heat will flow to the sample depends on whether the process is exothermic or endothermic [37].

Differential scanning calorimetry (DSC) is widely used for the characterization of materials with respect to phase transitions such as melting and crystallization. Recently, a novel technique known as Temperature Modulated DSC (TMDSC) has been introduced [1,2,3]. In TMDSC a periodic temperature modulation is superimposed on the constant heating or cooling rate of a conventional DSC measurement. METTLER TOLEDO has commercialized TMDSC as Alternating Differential Scanning Calorimetry (ADSC). It allows modulation with either simple waveforms such as steps or sawtooths ("Steady-State ADSC"), or with sinusoidal waveforms characterized by temperature amplitude AT and an angular frequency w, defined as 2p/P, where P denotes the period of the sine wave. In this latter case, the General temperature program, T(t), is given by

$$T(t) = T_0 + \beta_0 t + A_T \sin\omega t$$

where T_0 denotes the initial temperature, t the time and β_0 the underlying (average) heating rate.

Traditional DSC shows phase transitions, specific heat and chemical reactions in segments with linear heating and cooling rates or in isothermal temperature steps with high sensitivity and reproducibility. By varying the heating rates (cooling rates) in consecutive experiments, the sensitivity for individual thermal effects and sometimes also for the separation of overlapping effects can be influenced.

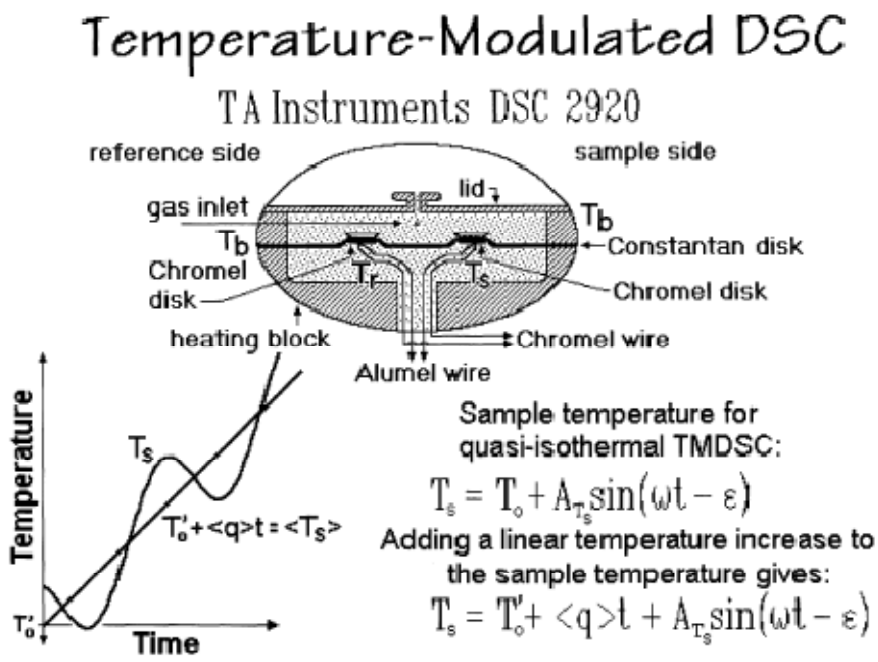


Fig: 21 Schematic diagram of TMDSC

For temperature-modulated DSC, on the other hand, the heating rates are varied by overlapping the underlying linear heating rates with a sinusoidal temperature modulation. The sample to be investigated is almost in equilibrium due to a linear rate which is mostly low; thermodynamic properties and transitions can therefore be accurately determined. At the same time, the sample is subjected to a non-linear temperature change which is relatively fast in comparison with the linear rate. Not only temperature-dependent but also time-dependent (kinetic) processes in the sample can therefore be detected with sufficient sensitivity.

Traditional DSC shows phase transitions, specific heat and chemical reactions in segments with linear heating and cooling rates or in isothermal temperature steps with high sensitivity and reproducibility. By varying the heating rates (cooling rates) in consecutive experiments, the sensitivity for individual thermal effects and sometimes also for the separation of overlapping effects can be influenced.

Thermal Behavior of Polymers

Glass Transition Temperature (Tg)

• At low temperatures, all amorphous polymers are stiff and glassy, sometimes called as the Vitreous State, especially for inorganic polymers. On Warming, polymers soften in a characteristic temperature range known as the glass-rubber transition region. The glass transition temperature (Tg), is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states[38]. Tg constitutes the most important mechanical property for all polymers. In fact, upon synthesis of a new polymer, the glass transition temperature is among the first properties measured. The following physical properties undergo a drastic change at the glass transition temperature of any polymer:

a) Hardness

b) Volume

c) Modulus (Young's module)

d) Percent elongation-to-break

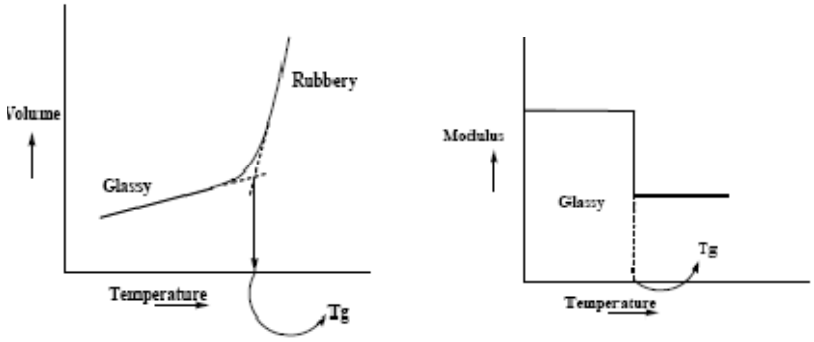


FIG- Represents the variation of Tg [12].

3.1 D Atomic force microscope (AFM)

The **atomic force microscope** (AFM) or **scanning force microscope** (SFM) is a very high-resolution type of scanning probe microscopy, with demonstrated resolution of fractions of a nanometer, more than 1000 times better than the optical diffraction limit.

The precursor to the AFM, the scanning tunneling microscope, was developed by Gerd Binnig and Heinrich Rohrer in the early 1980s, a development that earned them the Nobel Prize for Physics in 1986. Binnig, Quate and Gerber invented the first AFM in 1986.

BASIC PRINCIPLE

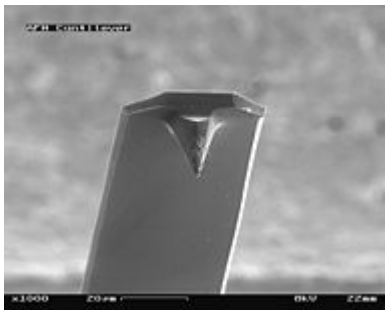


FIG 2 2 AFM Set-up tip [24].

The AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon nitride with a tip radius of curvature on the order of nanometers. When the tip is brought into proximity of a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law. Depending on the situation, forces that are measured in AFM include mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces (see magnetic force microscope, MFM), Casimir forces, solvation forces, etc. As well as force, additional quantities may simultaneously be measured through the use of specialized types of probe .Typically; the deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes. Other methods that are used include optical interferometry, capacitive sensing or piezoresistive AFM cantilevers. These cantilevers are fabricated with piezoresistive elements that act as a strain gauge. Using a Wheatstone bridge, strain in the AFM cantilever due to deflection can be measured, but this method is not as sensitive as laser deflection or interferometry.

3.1 E SCANNING ELECTRON MICROSCOPY (SEM)

The **scanning electron microscope** (**SEM**) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathodoluminescence), specimen current and transmitted electrons. Secondary electron detectors are common in all SEMs, but it is rare that a single machine would have detectors for all possible signals. The signals result from interactions of the electron beam with atoms at or near the surface of the sample. In the most common or standard detection mode, secondary electron imaging or SEI, the SEM can produce very high-resolution images of a sample surface, revealing details about less than 1 to 5 nm in size. Due to the very narrow electron beam, SEM micrographs have a large depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample.

Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample. For the same reason, BSE imaging can image colloidal gold immuno-labels of 5 or 10 nm diameter which would otherwise be difficult or impossible to detect in secondary electron images in biological specimens.

3.2 Experimental set-up And Materials

Materials

The unmodified epoxy resin (Araldide LY-556) based on Bisphenol-A and hardener HY- 951 an aliphatic primary amine (Ciba-Geigy) used as matrix and glass fiber was used for preparing the micro-composites for hygrothermal treatment.

. The same test was conducted with another matrix i.e. unmodified polyester resin. For cryogenic treatment laminated composites were prepared from woven and chopped glass fiber for ILLS testing. The fibre used was E-glass fibre treated with silane-coupling sizing system (Saint-Gobian Vetrotex).

3.2. A Hygrothermal Treatment

The specimens were fabricated using the conventional hand lay-up method. A plane mould was treated with silicon based releasing agent for easy removal of glass/epoxy micro-composites. A single strand of glass and carbon fiber was placed on the mould and the layer of catalyzed epoxy was poured on to it uniformly. Very light rolling was then carried out to remove any gas pockets if present and to uniformly distribute the epoxy resin throughout the composite. The micro-composites prepared were then cured at room temperature for 24 hours. Then the samples were treated in microprocessor controlled Brabender climatic chamber for hygrothermal conditioning. The samples were divided into six batches, they were hygrothermally treated for 10, 40, 60 and 100 hours in 95% RH and one batch remain untreated.

3.2 B FTIR spectroscopy analysis

FTIR analysis was performed in FTIR spectrophotometer interfaced with IR microscope operated in reflectance mode. The microscope is equipped with a video camera, a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector and a computer controlled translation stage, programmable in the x and y directions. The spectra were collected in the 4000cm-1 to 650 cm-1 region with 8 cm-1 resolution, 60 scans and beam spot size of 10µm- 100µm. The spectral point-by-point mapping of the interface of the epoxy cured composites was

performed in a grid pattern with the use of computer controlled microscope stage. Since the surface of the film was not perfectly smooth and its thickness was not uniform care should be taken to mount the sample such that a major portion of the plane was in the same focal plane. The FTIR imaging was performed in AIM-800 Automatic Infra red Microscope (SHIMADZU).

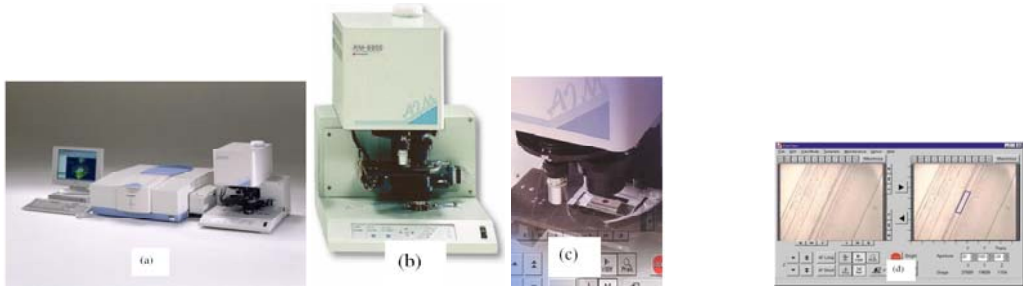


FIG 23 : (a) FTIR spectrophotometer, (b)-(c) AIM-800 Automatic Infra red Microscope, (d) 2-D view taken by the microscope equipped video camera.

There are certain limitations of refraction and reflection at the fibre surface in the spectroscopy that will finally affect the FTIR spectra of glass/epoxy composites. Due to this only a small percent of light reaches the detector. It is difficult to separate these optical effects from the samples. However these optical effects can be minimized by taking FTIR spectra over the same region of the micro-composites.

The gradient in the structure of the epoxy resin as a result of the cure process at the fiber/matrix interfacial region was monitored by FTIR imaging. Chemically specific images of the OH and the H–N–H groups near the interface region were obtained. These images suggest that there is a chemical gradient in the structure of the matrix from the fiber surface to the polymer bulk due to different conversions.

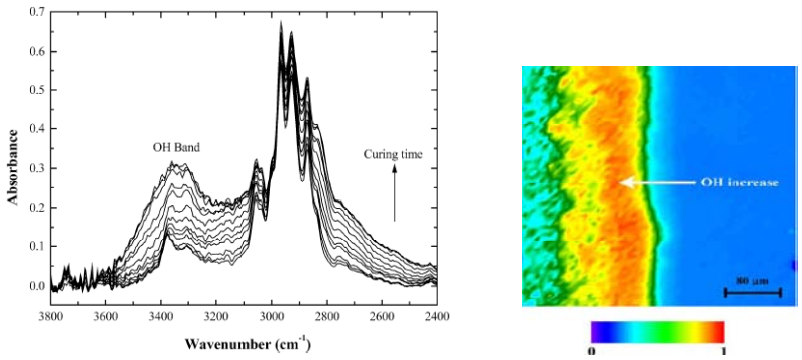


Fig-23.1 Evolution of the FTIR spectra for the epoxy–amine mixture as a function of the curing process.

3.2 C TMDSC ANALYSIS

The DSC measurements were performed on a Mettler-Toledo 821 with intra cooler, using the STAR software with Temperature Modulated DSC (TMDSC) module. The temperature calibration and the determination of the time constant of the instrument were performed by standards of In and Zn, and the heat flow calibration by In. The underlying heating rate of 10_Cmin-1 was used. In order to calibrate the heat flow signal, a blank run with an empty pan on the reference side and an empty pan plus a lid at the sample side was performed before the sample measurements. Standard aluminum pans were used. The experiments were performed in the temperature range from 40_C to 100_C.

Fig 24 . (a) Mettler-Toledo 821 with intra cooler for DSC measurements and (b) Reference-sample chamber

3.2 D SCANNING ELECTRON MICROSCOPE (SEM)

The SEM micrographs of as received powder, milled powder samples were obtained using the scanning electron microscope. The images were taken in both secondary electrons (SE) And back scattered electron (BSE) mode according to requirement. Microscopic studies to Examine the morphology; particle size and microstructure were done by a JEOL 6480 LV Scanning electron microscope (SEM) equipped with an energy dispersive X-ray (EDX) Detector of Oxford data reference system. Micrographs are taken at suitable accelerating Voltages for the best possible resolution using the secondary electron imaging.

FIG:23.2 JEOL JSM-6480LV scanning electron microscope.

3.2. E Flexural test (Short Beam Shear Test)

The short beam shear tests were carried out for first batch of samples immediately after exposure to cryogenic temperature. The former samples after exposure to room temperature and the untreated as-cured samples were tested in short beam shear test at room temperature. All the mechanical flexural tests were performed at 2, 50, 100, 200 and 500 mm/min crosshead speeds.

Then breaking load and strain at maximum load was measured from stress vs strain graphs for all the samples. An Instron1195 tensile testing machine was used to perform SBS tests in accordance with ASTM D 2344-84 standard. Multiple samples were tested at each point of experiment and the average value was reported.

FIG 25: Instron 1195

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Chapter – 4

Hygrothermal treatment

Thermal shock

Thermal spike

Results and discussions

CHAPTER-4

RESULTS AND DISCUSSIONS

4.1 HYGROTHERMAL TREATMENT

There are number of areas in which environmental effects have an important effect on the properties of polymeric composite. The level and rate of water uptake by a polymer composite are dependent on the atmospheric moisture content, the type of polymer, and the mechanism by which moisture is absorbed into the polymer[38]. Loss of performance is associated with physical and/or chemical changes that results from moisture uptake. The process of moisture absorption into polymer composite is often considered to be driven by simple Fickian diffusion. Since Fickian diffusion is a process in which the transport of the penetrant is a diffusion process driven by the penetrant concentration gradient[39]. If there are preferential sites within the matrix to which the water molecules may become bound, rather than remaining as free molecules or clustered groups, then this gives rise to dual mode sorption. Another important mechanism is hygroelatic swelling of the polymer as the constituent macromolecules rearrange to relieve the osmotic pressure of the penetrant. This leads to the penetrant moving into the polymer with a discontinuous concentration profile separating region of swollen, concentration-equilibrated and unswellon, zero-concentration polymer[40].

During the diffusion process, water molecules may form H bond with epoxy resin, consequently some of the water-water H bonds have to be compromised. The positive shift of O-H stretching spectra in the structure of epoxy resin as a result of hygrothermal process at the fiber/matrix interfacial region was monitored by FTIR-Imaging [41]. This reveals that, the interaction between water molecules and the carbonyl oxygen in the epoxy matrix and thus a weakening of the water-water H bonding. Besides that, the polar groups at the inner surface of free volume provide the bonding sites for water molecules, while the limited space of nanopores restrict the formation of water-water H bonding [42]. Chemically specific images of the OH group near the interface region were found. Change in FTIR spectra shows alternation and deviation of stoichiometry. Fig.20 shows the absorbance of the hydrogen-bonded O-H stretching band ($3600cm^{-1}$) increases.

The O-H absorption band is broad and strong this shows there is disappearance of the ring of epoxy. This happens from the centre of the glass fiber to the bulk of the polymer, where the O-H band increases from interphase region to the bulk region [43].The rest of the pixels shows the spatial distribution and contain spectra with similar evolution in their characteristic IR bands.

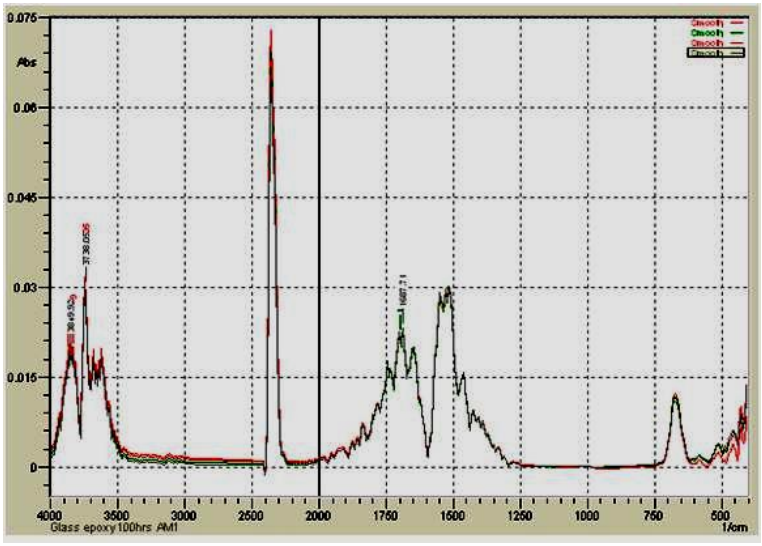
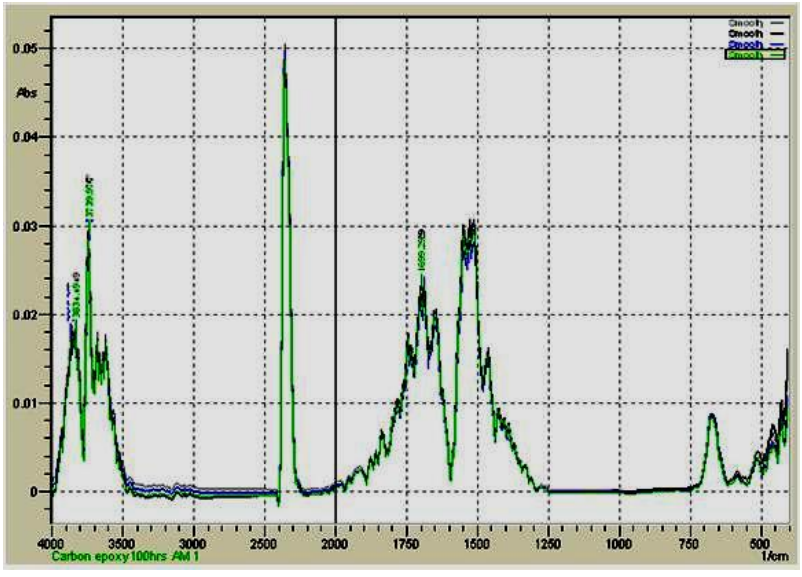


Fig 26: It presents the spectra in ambient temperature of glass/epoxy micro-composites



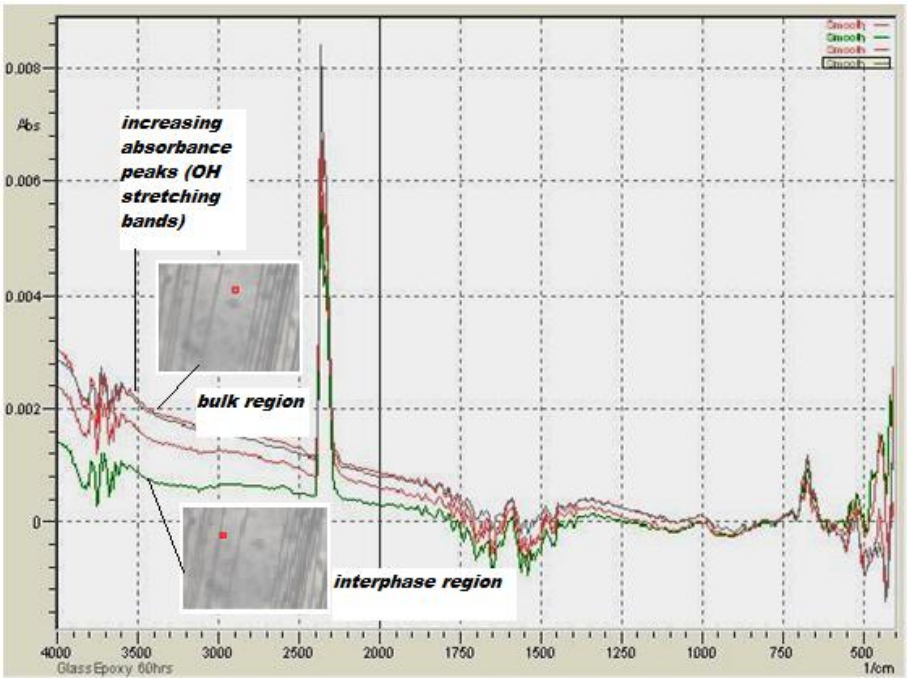


Fig 28 : It shows the shift of spectra of glass/epoxy micro-composites after hygrothermal treatment.

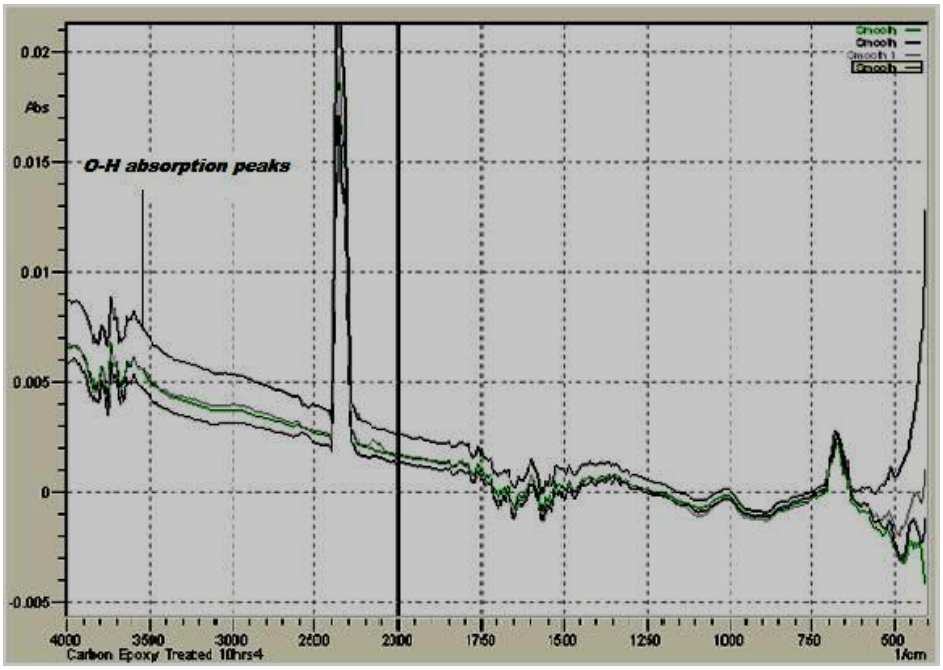


Fig 29: it shows the shift of spectra of carbon/epoxy after hygrothermal treatment.

ANALYSIS OF CARBON FIBER

It is generally true that fiber tensile modulus increases with increasing with increasing carbonization temperature. This is attributed to structural changes in the fiber, which has deleterious effects on its wettability by matrix resins.

Internal reflection FTIR Spectroscopy has been used to study the functional groups presents on the oxidized fiber surface. The larger size of the incident beam calls for novel experimental approaches[44].

The carbon surface was found to selectively absorb the tertiary amine catalyst and to modify the chemical state of the cured resin, apparently through the effects of absorbed water.

4.2 ATR-FTIR Analysis

Glass epoxy micro-composites

Changes of frequency, intensity, and shape of the water-related bands have been interpenetrated in terms of bound and free water (up to four different water species in some systems),water clustering, water orientation, and water networking. ATR-FTIR spectra have been quickly developed for studying the water diffusion behavior. The O-H vibration modes of liquid water lead to a very complicated vibration spectrum, complicated by both intermolecular and intramolecular hydrogen bonding. The ATR-FTIR spectrum of pure water and time-evolved spectra for water diffusion into an epoxy resin in the spectral range 3900-2800 cm^{-1}[45].

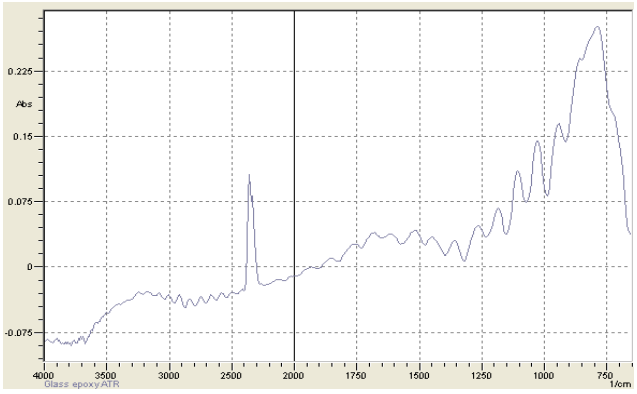
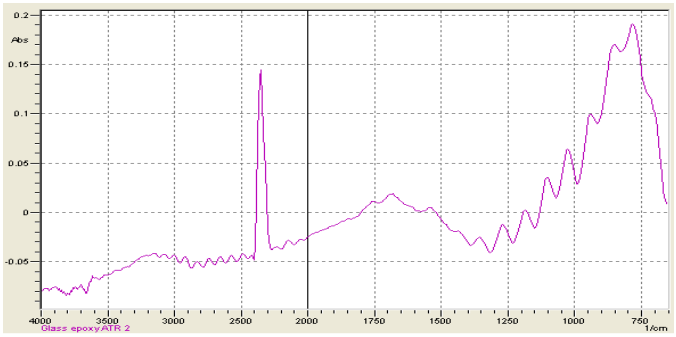


Fig 30 it shows carbon /epoxy micro-composite after hygrothermal treatment



Fig;31 shows glass /epoxy micro-composites.

4.3 Temperature Modulated DSC Analysis (TMDSC)

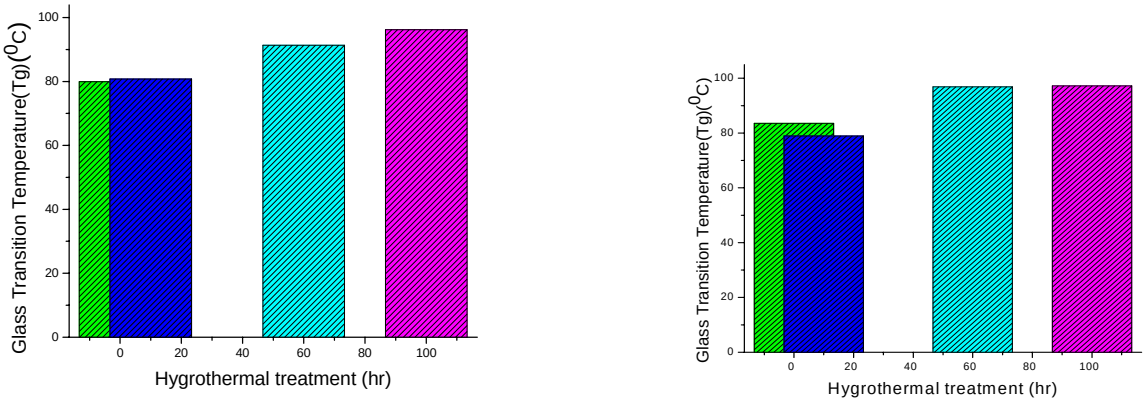


Fig:33 Schematic representation of hygrothermal treatment of glass and carbon epoxy micro-composites respectively showing Tg variation.

The physical cause of glass transitions of polymer are place change of molecular groups. Since the glass transition temperature (Tg) corresponds to a mobility change in a polymer and has a definite free volume associated with it, the jumping frequency of a segment is same magnitude for nearly all polymers. The Tg value usually decreases with ageing[46]. But when the ageing time was much less, an increase of Tg was comes in picture. This is may be increase of cross-link density of matrix which decreases the molecular mobility of the polymer. Another reason behind this, it may be due to reaction of moisture of water molecules with the hydroxyl group of the epoxy matrix resulting in the formation of a strong double hydrogen bond by replacing the existing covalent bond with the interface region[47]. The physical cause of glass transition of polymers is place change of molecular groups. Tg corresponds to a mobility change in a polymer and has a definite free volume associated with it.

The glass transition (Tg) value usually decreases with ageing, but when the aging time was much less, an increase of Tg was comes in picture which shown in Fig 23. This is may be increase of cross-link density of matrix which decreases the molecular mobility of the polymer. This may be due to reaction of water molecules with the hydroxyl group of the epoxy matrix resulting in the formation of a strong double H bond by replacing the existing covalent bond with the interface region/ may be due to formation of crack closure which form early in the absorption process [48]. In the TMDSC measurement, the structure through the Tg region is nearly in the quasi-equilibrium state [49].

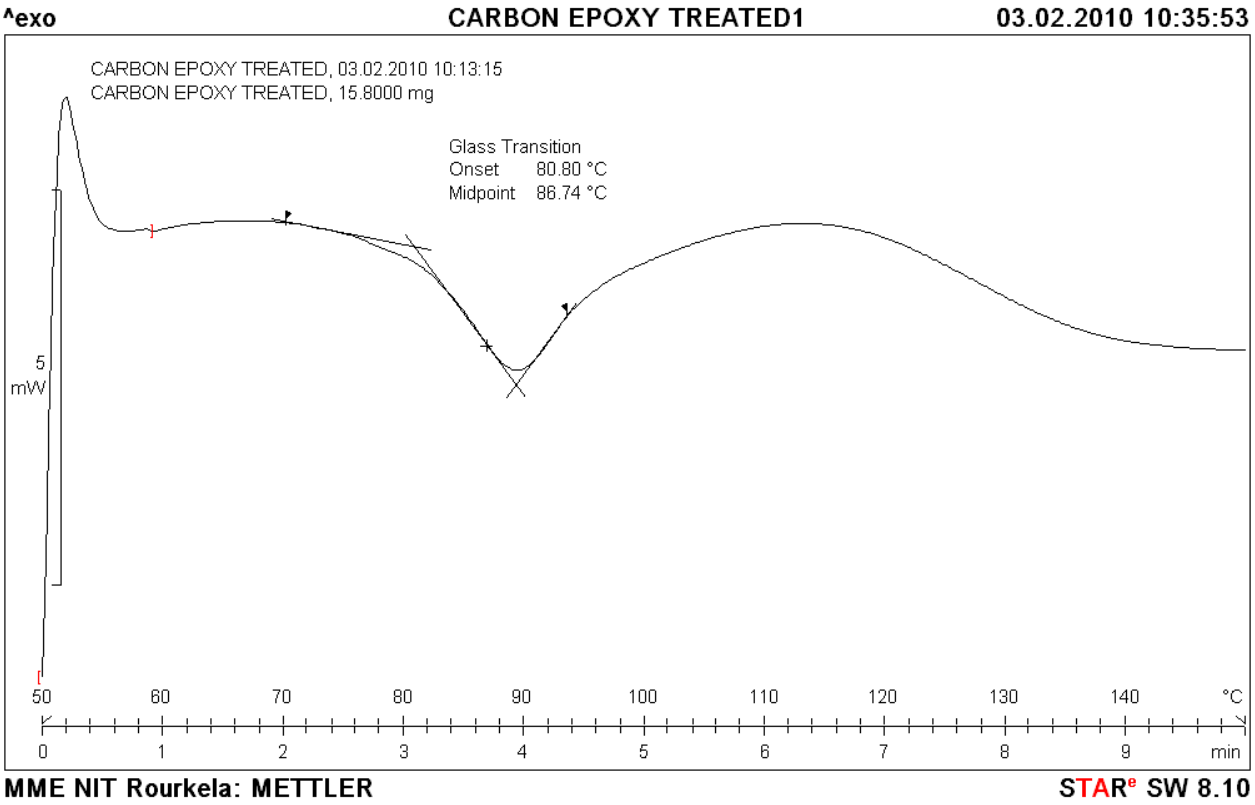


Fig 34: It shows the Tg value of carbon /epoxy

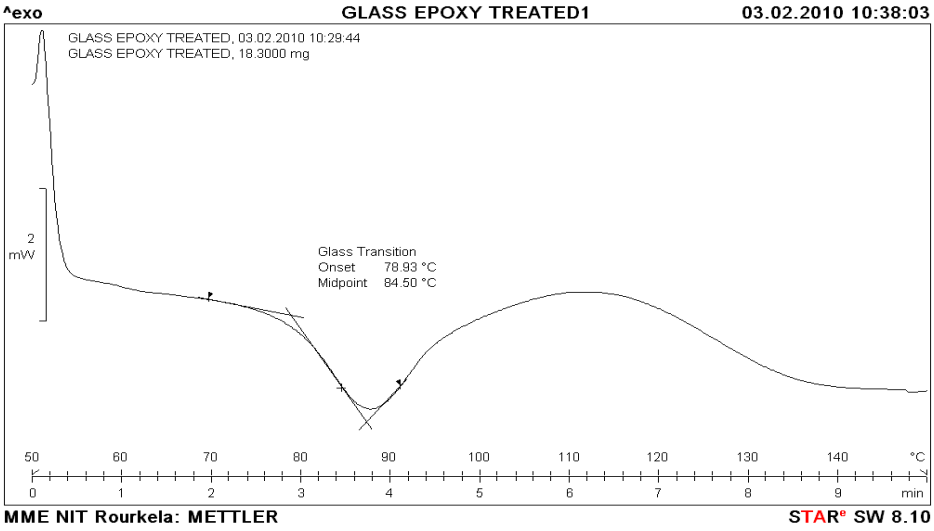
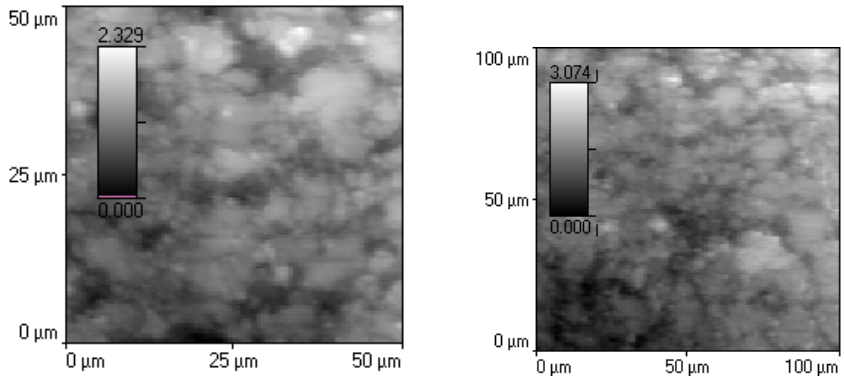


Fig 35: It shows the Tg value of glass/epoxy

4.4 Atomic Force Microscope (AFM) analysis

AFM has become an useful tool for characterizing the topography and properties of solid materials since its advent. Basically, AFM uses a sharp probe to scan across a surface. The probe-sample interactions are monitored depicting the maps of the material topography as well as those properties such as mechanical, electrical, and magnetic properties. In tapping mode AFM, the cantilever is excited into resonance oscillation with a piezoelectric driver. The cause of contrast in Tapping Mode AFM topography (also called height) and phase micrographs are rather complex. Height micrographs are recorded by maintaining a constant oscillation amplitude and recording the required vertical position of the scanner head at each (x,y) data point.

Thermal treatment increased the height difference, believed to be caused by matrix shrinkage resulted from additional cure under elevated temperature [50].



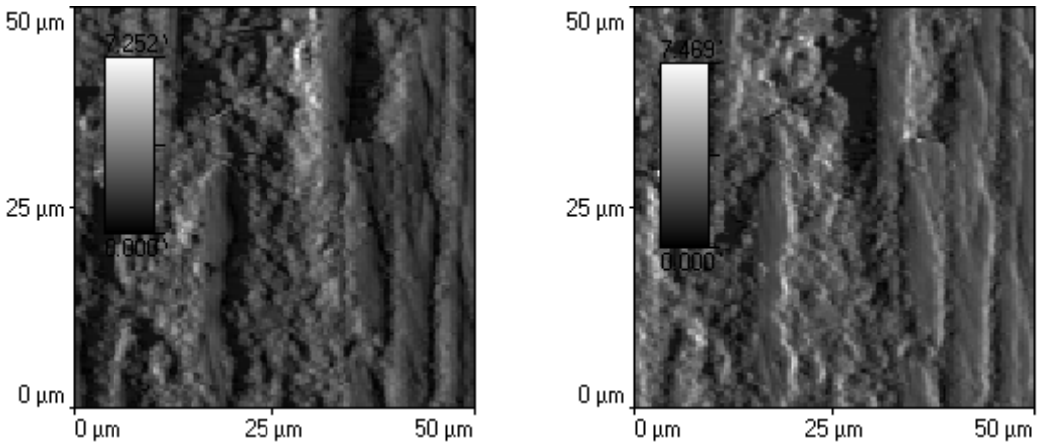


Fig 36- it shows the height image of the hybrid composite after thermal shock treatment.

4.4 Microscopic Interphase Analysis:

It is at the interfacial region where stress concentration develop because of difference in the thermal expansion coefficient between the reinforcement and the matrix phase due to loads applied to the structure and the time of curing shrinkage. Some degree of debonding at the interface region appears due to moisture absorption [51]. After hygrothermal treatment this curing stress converts to swelling stress. This swelling stress is related to the differential strain which created by the expansion force exerted by the liquid while stretching polymeric chains and molecules form disentanglement shown in Fig.37

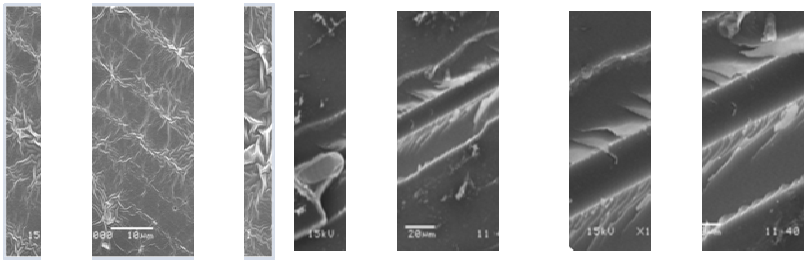


Fig 37 ; shows the swelling stress of glass/epoxy micro-composites.

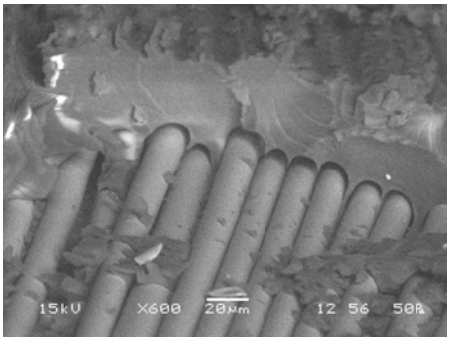


Fig 38: Fiber/matrix debonding

Interfacial debonding, caused by the large shear stress at the tip of the fiber end, can act to relieve the local stress. Therefore, the bond between fiber and resin must be sufficiently weak to fail in shear to relieve the local stress concentrations near a fiber break to avoid brittle failure [51].

On the other hand, the interfacial bond must be sufficiently high to allow effective stress transfer from the resin to the fiber in order to achieve a maximum tensile strength in composite [52].

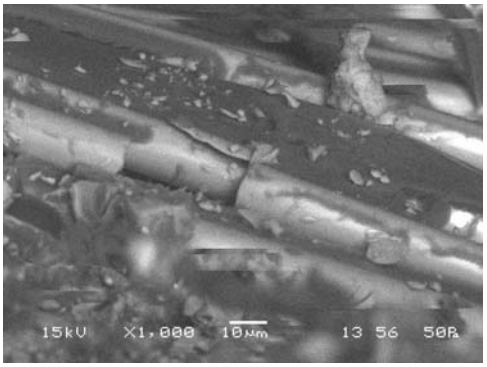


Fig 39; shows the fiber fracture

Fracture of fibers during processing / in service is generally an undesirable feature. Fracture in fibers, as in bulk materials, initiates at some flaw(s), internal /on the surface. In general, because of the high surface to volume ration of fibers, the incidence of a fiber flaw leading to fracture is greater in fiber than in bulk material. Very frequently, a near surface flaw such as a microvoids/ or inclusions is responsible for the initiation of fracture of fiber.

In polymeric fibers, the fundamental process leading to failure are chain scission /or chain sliding or a combination therof. One major problem in glass fiber is that of failure due to static fatigue. According to the chain-bundles model, if a fiber fractures, the matrix translates the load to the neighboring fibers in the composite. The stress concentrations at the broken fiber ends, unless dissipated properly, may induce failure in adjacent fibers and precipitate catastrophic failure of the composite [53].

4.5 *Assessment of mechanical behavior (implication of thermal spike)*

Hybridization provides materials designers with an added degree of freedom in tailoring composite to achieve a better balance of stiffness, strength, increased failure strain, better damage tolerances, improved ability to absorb impact energy and possibly a significant reduction in cost[54]. The structural integrity and lifetime performance of fibrous polymeric composite are strongly dependent on the stability of the fiber/polymer interfacial region. This region is the site of synergy in composite materials and its influence to overall mechanical properties is significant.

Thermal expansion coefficients in polymers are considerably high. Thus the interfacial de-bonding may occur under extremes of temperature. The cooling from high temperature to low temperature generally produces tensile stresses at the surface and compressive stresses in the interior[55]. They are also susceptible to crack initiation and propagation along the laminar interfaces in various failure modes. Thermal stresses caused by temperature gradient should be given special attention in many application areas. The presence of these stresses can result in matrix cracking. In an FRP composite, the fiber and the matrix have different coefficients of thermal expansions (CTE). Hence, excursions through the same temperature range results in differential expansion. This induces additional stresses at the fiber-matrix interface, thereby weakening the interfacial region.

The ILSS value calculated as,

$$ILSS=\frac{075P}{bt}$$

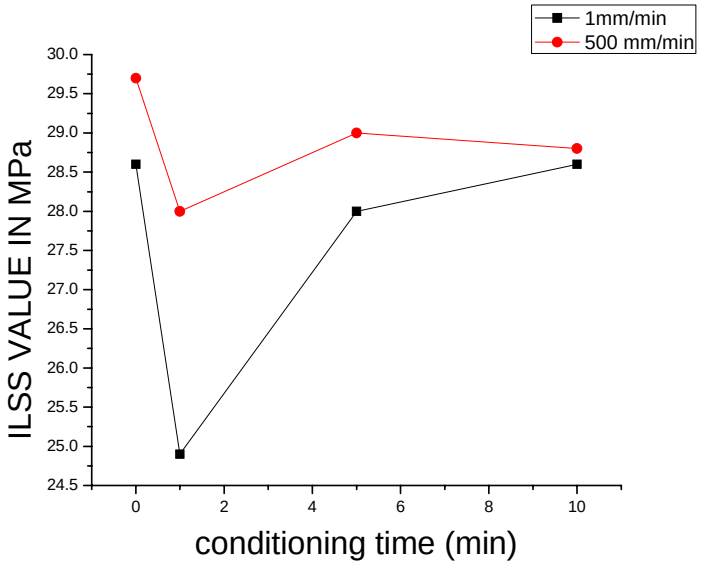


Fig 40: variation of ILSS value with respect of conditioning time at 150^0 C.

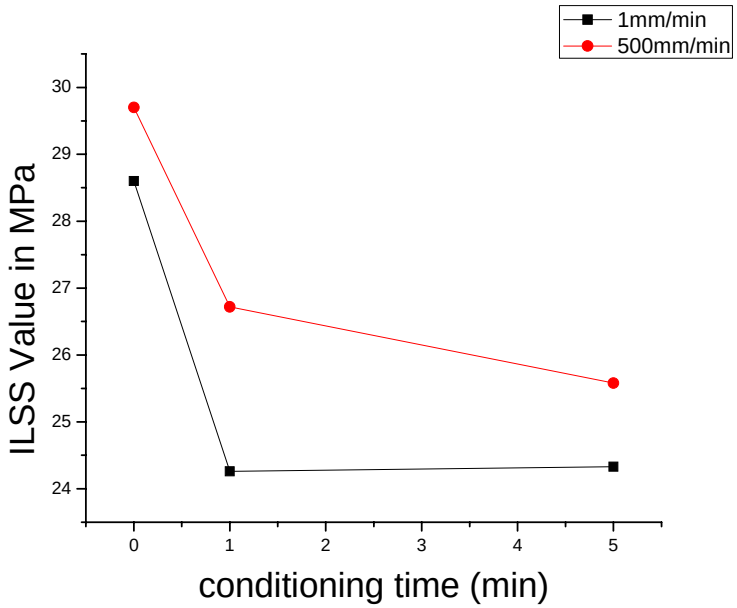


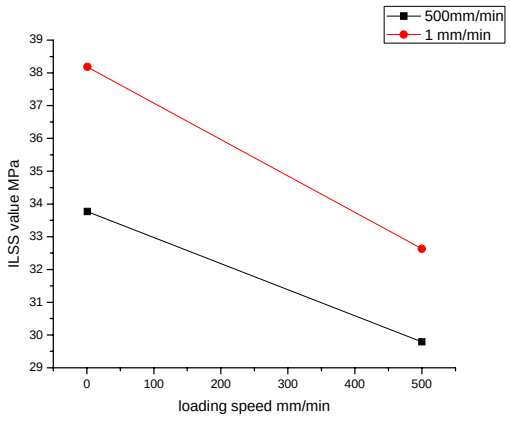
Fig41: variation of ILSS value with conditioning time at 200^0C.

Thermal spike at 150^0c temperature might possibly improve adhesion level at the interface. This effect is supposed to increase with less conditioning time. It is possibly attributed by surface chemistry principle at the fiber/polymer interface.

A better fiber/matrix adhesion will impart better properties such as ILSS and delamination resistance to a polymeric composite. A large thermal expansion mismatch between a fiber and polymer matrix can result in a quite possible debonding and matrix/interfacial crackings in polymer composites due to misfit strain at the interface. Thermal spiking carried out at higher temperature than those expected from kinetic heating could therefore be expected to produce a greater degree of permanent damage[56].

The bond strength depends on the quality of interfacial adhesion. The degree of cross-linking may increase during thermal conditioning. The high cross-linked networks have lower molecular mobility. Consequently, the mechanical behavior of these composites is different from the composites without any form of thermal conditioning. Fracture of epoxy involves breaking of covalent bonds in the chains. So it undergoes ductile fracture at high temperature. At temperature, above glass transition temperature (Tg) ,at least at slow to moderate rates of deformation, the epoxy is soft and flexible and is either an elastomer / a very viscous liquid[57]. The diffusion rate of segments increases approximately linearly with increase of temperature.

IMPLICATION OF THERMAL SHOCK



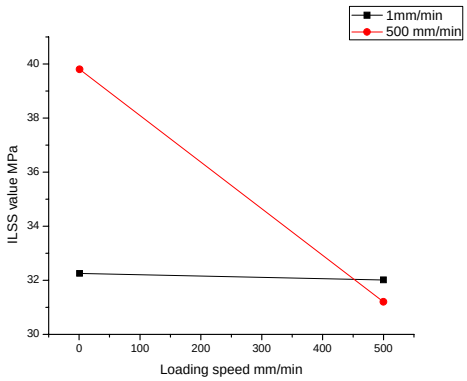


Fig 42 variation of ILSS value after thermal shock treatment.

Thermal shock is performed to determine the resistance of the part to sudden changes in temperature.[58]. The parts undergo a specified number of cycles, which start at ambient temperature. The parts are then exposed to an extremely (low/high) temperature, and within a short period of time, exposed to an extremely high (or low) temperature, before going back to ambient temperature[59]. This treatment is the result of a thermal gradient, which refers to the fact that temperature change occurs in an uneven fashion[60]. This is due to expansion of the molecular structure of an object, due to weakening of the bonds which hold the molecular in formation. The conditioning at 60 C temperature may impart better adhesion at the fiber/matrix interface by a surface chemistry mechanism[61]. The fall in ILSS value at a higher number of cycle is possibly due to a greater misfit strain effect, that leads to more debonding at the fiber/matrix interface.

CONCLUSION

In this work the process of water uptake kinetics in glass/epoxy micro-composite have been monitored. The experiments were carried out by TMDSC, FTIR-Imaging, AFM, and SEM to complementary follow the process in the whole composite system. TMDSC results where there is a marked increase in Tg value, because of formation of double H bond with the epoxy system by water molecules. The increase in absorbance peaks of OH stretching bands at the interphase was found in FTIR-Imaging. Thermal treatment increased the height difference, believed to caused by matrix shrinkage resulted from additional cure under elevated temperature. There is a wide variation of mechanical behavior needs to be supported by the understanding of the science at the fiber/polymer interface region. The importance of this investigation is to explore the interfacial chemistry which decisively controls the integrity and consistency of mechanical performance.

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